Progress Report

Chemical Research in Nuclear Submarine Atmosphere Purification

Edited by

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PREVIOUS REPORTS IN THIS SERIES

"The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," R. R. Miller and V. R. Piatt, editors, NRL Report 5465, Apr. 21, 1960

"Annual Progress Report, The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," V. R. Piatt and E. A. Ramskill, editors, NRL Report 5630, July 14, 1961

"Second Annual Progress Report, The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," V. R. Piatt and J. C. White, editors, NRL Report 5814, Aug. 29, 1962

"Third Annual Progress Report, The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," H. W. Carhart and V. R. Piatt, editors, NRL Report 6053, Dec. 31, 1963

"Fourth Annual Progress Report, The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," V. R. Piatt and L. B. Lockhart, editors, NRL Report 6251, Mar. 23, 1965

"Fifth Annual Progress Report, The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," A. L. Alexander and V. R. Piatt, editors, NRL Report 6491, Jan. 11, 1967

"Sixth Annual Progress Report, The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," R. R. Miller and V. R. Piatt, editor, NRL Report 6722, June 18, 1968

CONTENTS

ABSTRACT

This progress report supplements NRL Reports 5465 of Apr. 21, 1960; 5630 of July 14, 1961; 5814 of Aug. 29, 1962; 6053 of Dec. 31, 1963; 6251 of Mar. 23, 1965; 6491 of Jan. 11, 1967; and 6722 of June 18, 1968, which provided a comprehensive review of the past and present research and development effort of NRL on the atmospheric habitability of submarines. At present, emphasis is being devoted almost exclusively to nuclear-powered submarines, although an increasing effort is being applied to SeaLab, Man-in-the-Sea, and other tasks of the Deep Submergence Systems Project. Considerable progress has been made in developing both laboratory and shipboard methods of sampling, analysis, and control, but major shipboard analytical equipment continues to be of marginal quality. Some of the topics covered in the present report include a fire-retardant and nontoxic paint system for application when necessary during submergence, atmospheric contamination with a cleaning solvent, the NRL Total Hydrocarbon Analyzer, catalyzed combustion of various types of atmospheric contaminants, and CO_2 absorption properties of some new amines.

PROBLEM STATUS

This is an interim report; work is continuing on all phases of the program.

AUTHORIZATION

PROGRESS REPORT

CHEMICAL RESEARCH IN NUCLEAR SUBMARINE
ATMOSPHERE PURIFICATION

SUMMARY OF PROGRESS

The first report in this series (1) and subsequent annual progress reports (2-7) provided historical, status, and progress reports on submarine air-replenishment equipment and supporting research. Due to the changing nature of the overall research and development effort in the atmosphere purification area, and particularly to the organizational changes in the program at NRL, the timing, title, and purposes of this periodic report have been altered. Intermittent hazards in operational submarines continue to divert and direct research and development resources, and long range objectives of maximizing the efficiency of shipboard equipment are still necessary goals. The basic hope for continued significant progress now seems to lie in the Proposed Technical Approach (PTA) prepared by NavSec and approved and forwarded by the Naval Material Command to the Chief of Naval Operations.

A number of fluorocarbons (normally containing chlorine as well as fluorine) have been found previously in nuclear submarine atmospheres, particularly refrigerants and solvents. Chapter 7 of our last progress report (7) contained a table of such fluorocarbons which were found to decompose fairly readily when passed through a bed of Hopcalite at elevated temperatures, forming toxic and corrosive compounds. One of these, Freon-113 (also known as Freon TF and Freon PCA), was investigated in low concentrations, and a current study (Chapter 1 of this report) indicates that much higher concentrations may be encountered, particularly in oxygen banks which have been cleaned with the material. Of special concern should be certain efforts to increase the use of Freon-113 as a cleaning compound in ships without having insured adequate safety by subsequent cleanup.

The catalytic combustion studies discussed in the same Chapter 7 of our last progress report have been extended, with emphasis on atmosphere contaminants at low concentrations (Chapter 2 of this report). Recent studies have covered CO in hyperbaric atmospheres (of special interest to SeaLab III and other Man-in-the-Sea ventures), the effect of three materials (n-decane, NTU-4 (a paint thinner), and R-12) on the ability of Hopcalite to oxidize CO, and the oxidation of thiophene as a representative of typical sulfur compounds in petroleum products. Not discussed in detail in Chapter 2 is the oxidation of Otto Fuel in the catalytic burner to produce nitrogen dioxide (NO_2), a compound with potentially serious results if found in even low concentrations in the nuclear submarine (8).

The commercial production of the NRL Total Hydrocarbon Analyzer, anticipated in Chapter 3 of the last report, is now in process (Chapter 3 of this report). Development of the instrument is completed, but some modifications of the initial commercial items are necessary. Production of the 119 units by the three manufacturers is not yet complete.

Previous studies of the gas chromatographic-rapid-scanning mass spectrometric system for analyzing submarine atmospheres (Chapter 2 of the last report) have indicated both advantages and disadvantages of the system. Recent studies (Chapter 4 of this report) demonstrate primarily the advantages of the techniques involved and the highly sophisticated improvements being made by NRL. Although not covered by the present chapter, the Proposed Technical Approach includes a realistic appraisal suggesting that a coming

mass spectrometric technique coupled with a computer could be incorporated in a shipboard apparatus for maximum effectiveness.

Continuous studies of various CO_2 absorbent systems have been important since it was found that the degradative properties of monoethanolamine (MEA) and the operating difficulties with the shipboard CO_2 scrubber combined to indicate the desirability of eventually replacing MEA and/or the scrubber. The additional requirement imposed by BuMed to lower the effective CO_2 concentration to 1/2% increased the importance of the CO_2 absorbent and CO_2 scrubber research. Chapter 5 of this report covers some of the significant studies on potential MEA replacements, and although three-component mixtures appear to provide the most hope, Sulfolane seems to be the best individual compound studied. The success of Sulfolane accentuates the importance of the catalytic combustion studies on thiophene, another sulfur compound, already discussed as studied in Chapter 2.

Also of continuing interest as CO_2 absorbents are molecular sieves, which have had continual reference in this series of reports and have been extensively studied by NASA and the British. Recent studies on the effect of atmospheric contaminants, such as Freons, on molecular sieves are reported in Chapter 6. Despite somewhat negative results from these studies, largely due to the extreme conditions employed in this study, molecular sieves remain high on the list of potential CO_2 removal systems, although invariably with the prospect of problems with regeneration, power, and volume.

This series of reports has also periodically included studies on potential substitutes for existing paint systems for painting in submerged nuclear submarines. The imposition of a fire-retardant capability has complicated the research efforts, but an obviously satisfactory solution has been obtained, as discussed in Chapter 7. Difficulties are being experienced, however, in arranging for field application of the new paint system in an operational nuclear submarine, and the delay of over a year and a half to date shows a need for the Naval Ship Engineering Center to take immediate action in arranging for field tests.

The need for emergency sampling equipment, i.e., for sampling when instruments or circumstances indicate that a serious atmospheric problem is present, has been recognized for several years (9-11). No action apparently has been taken since NRL submitted its latest letter report (12) to NavSec listing suggested specification requirements for the stainless-steel sampling bottles and the oil-free compressor, which are needed to collect compressed atmosphere samples.

Among several troubleshooting projects by NRL have been two investigations of atmospheric contamination resulting from the use of specialty papers. The latest study (13) covered an electrochemical recorder paper for use on the NR-1 and determined that adequate ventilation during use, coupled with subsequent isolation or sealed storage of papers after use, should reduce potential hazards from component aromatic hydrocarbons to negligible values. In several instances the new Mark V Atmosphere Analyzer has failed to operate properly due to the use of the contaminated carrier gas—helium. Efforts were then initiated to develop instrumentation to determine and eliminate such contamination before the use of helium in the analyzer. Eye irritation was experienced in the engine room of USS Puffer (SSN 652) during the first three sea trials and the INSURV (Board of Inspection and Survey) trial. Representatives from NRL and NavSec investigated the problem aboard ship and decided the most probable source was the lube oil preheater system, a situation remarkably similar to that experienced during the sea trials of the USS Snook (SSN 592) built by the same shipyard 8 years ago. The trouble with the Puffer was corrected in time for the ship to be accepted by the Navy on schedule.

Widespread deterioration of rubber shock mounts was observed during 1968 in a number of the newer ships. The symptoms indicated ozone cracking as the cause, and

measurements aboard six of the ships indicated the total oxidant level to be approximately ten times higher than the permitted amount. The ozone analysis was performed primarily by NSRDL (Annapolis) personnel using the NRL ozone meter and tube tests. With NRL and NSRDL (Annapolis) providing technical support to NavSec, suitable modifications have been made to the electrostatic precipitators to ameliorate the problem. As a side note, no medical difficulties were apparently encountered despite the ozone concentration exceeding the "safe" limit by a factor of ten, but the symptoms may possibly have been masked by other factors (no medical officers were aboard the ships to compare symptoms during tactical operations).

The incomplete evaluation of the Ionics, Inc., ion-exchange, ten-man prototype equipment for the generation of O_2 and absorption of CO_2 appears to conclude consideration of this entire system. It will take both additional funding and engineering initiative to complete a proper development and evaluation of the system.

Over 2 years ago, it was noticed aboard several of the ships that the Mark IV CO/H_2 burners had operating temperature variations beyond both the minimum and maximum permitted, and preliminary NRL studies provided stopgap corrections as well as indications that the airflow in the burners varied considerably from specifications. Recent data from NSRDL (Annapolis) on an operational CO/H_2 burner indicate that the temperature and air variations are even greater than previously anticipated, indicating major modifications are required. This is particularly true because of the observed phenomena that operation at temperatures greatly exceeding 600°F tends to increase the decomposition of solvents, refrigerants and other materials to yield corrosive compounds, whereas operation much below 600°F leads to insufficient oxidation of aliphatic and toxic aromatic compounds as well as assisting in the formation of still other compounds that are worse than the original atmospheric components.

A number of untoward events involving problems with CO and nitrous oxide (N_2O) still occur on submarines using the Mark III Atmosphere Analyzer. These problems have been the subject of considerable correspondence and reporting in the past and stem primarily from the analyzer giving a concentration of CO much higher than the permitted limit of 25 ppm, when the actual concentration rarely exceeds the limit by more than 5 ppm. The difficulty is due to a "crossover" sensitivity of the CO infrared channel on the Mark III to N_2O, and the concentration of the latter is often as high as 15 ppm without a hazard being present. If, however, the N_2O concentration rises to 20 or 25 ppm, it is an indication of an excessive amine concentration in the atmosphere, and the CO_2 scrubber is suspected. Often, changing the amine in the CO_2 scrubber has decreased the CO reading on the Mark III Analyzer. The original problem, moreover, is often compounded by shipboard personnel believing the nitrous gas detector tube is for nitrous oxide, N_2O, when it is actually for nitric oxide, NO, and nitrogen dioxide, NO_2. Further, the only semi-reliable detector tube for CO is the Bacharach Monoxor, and it is hard to decide whether to believe this tube or the Mark III Analyzer when the readings are different. The possibility is not eliminated that the CO reading can rise above normal for reasons of real concern.

Experience with the improved infrared sources and detectors for the Mark IV Atmosphere Analyzer indicates in general that most quality control problems have been corrected and that the frequency of analyzer repair has been lessened. A close watch must still be maintained on availability, proper storage, and recertification of spare parts.

Due mention should be made of some of the personnel and organizational changes in the habitability research and development program. Of considerable impact is the recent retirement of Dr. Franklin S. Thomas of NRL, who has been contributing to the solution of submarine atmosphere problems for 31 years and who has left his hallmark on the Mark I, II, III, IV, and VI Atmosphere Analyzers, as well as on the CO/H_2 burner and

various backup analytical instruments. Dr. William A. Zisman, Superintendent of the Chemistry Division at NRL, assumed a different research role in 1968 as Head of the Laboratory of Chemical Physics. He was succeeded as Superintendent of the Chemistry Division by Dr. Ronald E. Kagarise, who, in previous service at NRL, was involved in atmospheric habitability through infrared analyses and monitoring of the scientific reliability of the Mark IV Atmosphere Analyzer. NavSec has recently also seen a significant change, that of Sydney Baken leaving as the Code 6151 program manager to become a NavMat program manager. He has been replaced by Philip Ross, formerly Mr. Baken's assistant and an ex-habitability chemist at NSRDL (Annapolis).

The format of the quarterly habitability meetings (reviews) at NRL has also changed, with 1969 seeing the substitution of semiannual reviews. Previous reviews were usually limited to NRL chemists as the formal speakers, but medical, NavSec, NSRDL (Annapolis), and other speakers are now giving prepared talks. This review plus the NRL quarterly progress reports (14) represent the major coordination efforts of the overall nuclear submarine atmospheric habitability program. It is emphasized that the semiannual review is still informal enough that minutes are not kept, there is no subsequent report of the meeting, and attendance is limited to representatives of naval activities and submarines plus other U. S. government officials with a need to know.

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Chapter 1

ATMOSPHERIC CONTAMINATION
WITH A CLEANING SOLVENT

F. W. Williams and J. E. Johnson

INTRODUCTION

Since the beginning of the nuclear submarine program, NRL has been interested in the control of atmospheric contaminants. Of prime importance is the origin of these contaminants, whether they are knowingly or unknowingly introduced into the atmosphere. In many cases, a particular compound does not of itself constitute a toxicity or a materials problem, but the decomposition products which result when this compound passes through the CO/H_2 burner might cause a problem. This is particularly true in the case of chlorinated compounds (1), which, when passed through the CO/H_2 burner, produce hydrochloric acid (HCl) (2-5). Hydrochloric acid is deleterious not only because of toxicity but also because of its corrosiveness to materials.

Another continuing problem in atmosphere control is the use of various cleaning solvents in submarine upkeep and overhaul. One particular solvent that is finding widespread usage is 1, 1,2-trichloro-1,2,2-trifluoroethane, whose short commercial name is Freon-113, but it is also purchased by the Navy for cleaning purposes under the trade names of Freon-TF and Freon-PCA. The main distinction between the names is the purity – Freon-PCA being the better grade. Freon-PCA is approved for use in cleaning oxygen systems, whereas in nitrogen systems the Freon-TF will suffice.

In recent years this solvent, which we will refer to as Freon-113, has been applied to the cleaning of such critical systems and components as oxygen banks of submarines, flexible hoses for use by divers, and motor generator sets in submarines. NRL has participated in several evaluations of these applications in terms of residual solvent vapors in closed systems and the effect of the solvent on materials. This report contains a brief, overall summary of the findings in these situations.

EXPERIMENTAL PROCEDURES

The samples received for evaluation were gas samples taken from high-pressure gas systems or directly from atmospheres such as in nuclear submarines. The gas samples were analyzed with a MT 220 MicroTek Gas Chromatograph equipped with a Dohrmann Microcoulometric Detector, which is specific for chlorinated and brominated compounds. In addition, some of the atmosphere samples were analyzed for Freon-113 using the NRL Total Hydrocarbon Analyzer. A general gas chromatographic procedure which can be used for the analysis of Freon-113 can be found in Ref. 6.

RESULTS

Cleaning of High-Pressure Gas Systems

The cleaning solvent, Freon-113, was first called to the attention of NRL as a serious problem when it was introduced into the cleaning procedure for oxygen banks aboard

nuclear submarines. It was found that without a concentrated effort by the shipyards through a series of nitrogen purges and evacuations the Freon-113 remained in the oxygen banks (6).

Figure 1 shows the possible overall submarine contamination by Freon-113 in the atmosphere if the oxygen banks were contaminated with 12 ppm of Freon-113. This curve takes into consideration normal submarine operating procedures. Based on the experimentally determined rate of conversion of Freon-113 in the CO/H_2 burner (3), Fig. 2 shows the production of hydrogen chloride (HCl) (6).
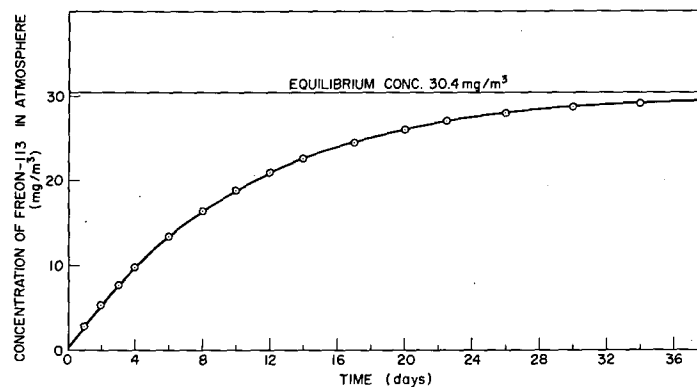

Fig. 1 – Possible overall submarine contamination
by Freon-113

Fig. 2 – Production of hydrogen chloride
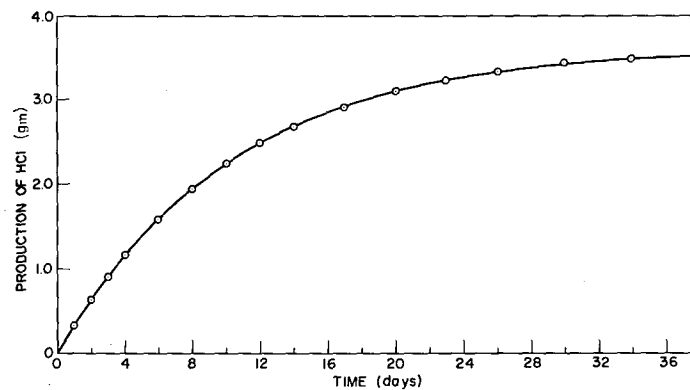from Freon-113

Cleaning of Motor Generators

The Naval Ship Engineering Center, Philadelphia Division, developed a procedure to clean motor generators on fleet submarines with Freon-113. This cleaning technique has been carried over to nuclear submarines. More specifically, a motor generator on board the USS Stonewall Jackson, SSBN 634, was cleaned with Freon-113. The liquid Freon-113

was allowed to empty into the bilge, where it was dispersed by the water in the bilge and subsequently pocketed due to its physical properties, thus becoming a source of "air" pollution (7). If the bilge had been dry, the Freon-113 could have been wiped up immediately and thus would not have become an atmosphere problem.

Until recently, most shipyards, tenders, and submarines had no way of monitoring the concentration of Freon-113 in the atmosphere of a submarine. As the Total Hydro-carbon Analyzer becomes available to the ships' forces, they will have a means of monitoring the concentration of Freon-113 in the atmosphere.

These analyzers are being procured for installation aboard each nuclear submarine. However, no provision has been made to provide the Total Hydrocarbon Analyzer for other ships or shore facilities. Some shipyard laboratories have been authorized to procure gas chromatographs for general use which can be adapted to this purpose quite readily.

Cleaning of Flexible Hoses

A high-pressure nylon-lined hose from SeaLab III preliminary operations was sub-mitted to NRL for evaluation (6) after it had been cleaned with Freon-113. The hose exhibited a high rate of outgassing of Freon-113 even after purges, evacuations, and heating for a period of 24 hours. The findings demonstrated that nylon will absorb highly and is incompatible with Freon-113. The Freon-113 also weakened the hose, causing leakage.

Discussion

Cleaning with Freon-113 in all-metal systems should be highly efficient as long as there is adequate means of removing the cleaning solvent. Based on experiences with several nuclear submarines, three nitrogen purges and evacuations at the termination of the cleaning procedure of high-pressure systems seem adequate to remove the Freon-113. However, the number of purges and evacuations required could vary with the system con-figuration and local conditions, particularly ambient temperature. Thus, the system should always be checked following the cleaning procedure to make sure it is free of Freon-113. For the most part, Freon-113 is not compatible with synthetic materials, and its compatibility in any nonmetallic system should be ascertained before using in such a system. In any event the cleaning solvent should not be emptied into the submarine indiscriminately.

The use of Freon-113 for cleaning diver's hoses and other breathing equipment must be carefully monitored to show the absence of residual solvent. The very small free volume of a diver's breathing system, compared to that available even in nuclear sub-marines, enhances the concentration of Freon-113 in his atmosphere. Diver's gear often contains nonmetallic parts which require serious evaluation as to compatibility with this solvent before using, as was emphasized earlier.

The level of Freon-113 in the oxygen banks at the termination of the nitrogen flush-ing procedure has been set by NavSec, Code 6154E, at 10 ppm by volume in the nitrogen prior to pressurization with oxygen. This amounts to about 0.33 ppm by volume when the oxygen banks are fully pressurized with oxygen. The level of Freon-113 in nuclear submarine atmospheres under closed boat conditions should not exceed 10 ppm based on the corrosion limits set for other compounds containing three chlorine atoms (8). For pressurized atmospheres, no guidelines have been set for Freon-113 concentration limits

However, since no data are currently available for the toxicities of solvent vapors under hyperbaric conditions, it would be prudent to keep the concentration of Freon-113 at the lowest possible level.

RECOMMENDATIONS

1. Prior to using Freon-113, the compatibility of the solvent with materials with which it will come in contact should be ascertained to prevent possible deleterious effects on the functional performance of the materials.

2. In any use of Freon-113 on board nuclear submarines, provisions should be made to recover the liquid Freon used with subsequent removal from the interior of the submarine.

3. Any Freon-113 that is spilled in the interior of a submarine should be immediately wiped up and disposed of exterior to the submarine.

4. Tubing of a material such as copper or Teflon, which is compatible with Freon-113, should be used to transfer the solvent.

5. When using Freon-113 in large quantities in enclosed spaces, auxiliary air-breathing devices should be used.

6. The level of Freon-113 in the nuclear submarine atmosphere should not exceed 10 ppm by volume under closed boat conditions.

7. While a submarine is underway, an emergency procedure similar to that used for Freon-11 spills (9) should be effective for controlling Freon-113, if the concentration of the latter exceeds 10 ppm.

8. An adequate test method, such as gas chromatography (e.g. with the Total Hydrocarbon Analyzer) or its equivalent, should be used to assure that a system is free of Freon-113 after this solvent is used for cleaning.

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Chapter 2

HOPCALITE-CATALYZED COMBUSTION OF ATMOSPHERIC
CONTAMINANTS AT LOW CONCENTRATION

James K. Musick

INTRODUCTION

In previous work at NRL, several types of compounds have been studied to determine the nature and extent of their decomposition over Hopcalite catalyst at 315°C (600°F). The experimental work employed a small-scale catalytic burner and a variety of compounds selected on the basis of their actual and potential presence as contaminants in closed atmospheres, such as those of submarines and the SeaLab habitat. This work has shown that, in addition to CO and H_2, most hydrocarbons and oxygenated compounds burn readily over Hopcalite at 315°C (600°F). The lower hydrocarbons, notably methane, are resistant to oxidation. All the nitrogen compounds studied, including ammonia, pyridine, morpholine, monoethanolamine, and propylene glycol dinitrate (PGDN), burned readily and produced appreciable amounts of the oxides of nitrogen. Nitrous oxide (N_2O) was produced from all compounds studied except PGDN, which generated nitrogen dioxide (NO_2). Aerosols of dioctyl phthalate and lubricating oil were completely oxidized, as were high concentrations of triarylphosphate ester (TAP) aerosol (c.a. 30 $\mu g/1$). In oxidizing the latter compound, the phosphate was retained on the catalyst, but this retention did not harm the catalytic activity toward hydrocarbons. Organic halogen compounds in air, when passed over Hopcalite catalyst, ranged in degree of decomposition at 600°F from slight in the case of R-12 (CCl_2F_2) to virtually complete with methyl chloroform (CH_3CCl_3). Sulfur hexafluoride (SF_6) was stable in an air stream passed over Hopcalite catalyst at temperatures as high as 425°C (797°F).

Recent work using Hopcalite catalyst includes studies of the oxidation of CO under hyperbaric conditions and in atmospheres that were largely helium. Also, the oxidation of CO has been studied in the presence of relatively large concentrations of n-decane, a paint thinner, or R-12. A third phase of the recent work has been concerned with the catalytic combustion of thiophene, C_4H_4S, which was selected for the preliminary studies of sulfur compounds in the CO/H_2 burner.

Carbon Monoxide in Hyperbaric Atmospheres

The presence of CO is believed to be the cause of headaches reported by the occupants of SeaLab II, particularly in the latter part of that experiment. By subsequent analysis of atmosphere samples taken during the SeaLab II operation, it was established that the CO concentration had built up to undesirable levels, a measured maximum of 30 ppm (1). Consequently, it was of considerable interest to devise an effective system for the removal of CO which could be used in further operations of this type. Hopcalite was chosen to be studied as the oxidation catalyst because of its long history of successful performance in the atmosphere purification systems of nuclear submarines.

The experimental apparatus used is shown in Fig. 3. It consisted of a pressurized cylinder containing the gas mixture, a pressure regulator, the catalytic burner, cooling condenser, pressure gage, flow control valve, and flow meter. These units were connected in series by means of 1/4-inch stainless-steel tubing and fittings. In operation, a gas mixture containing CO passed from the cylinder through the burner where it was exposed to the Hopcalite catalyst. After leaving the catalyst bed, the gas was cooled by a water condenser and passed through the flow meter. The pressure regulator and the flow control valve permitted the operating pressure and gas flow rate through the system to be set independently at various constant values. The burner was a 29-inch length of stainless-steel tubing 1-1/4 inches in diameter. The lower part of the vertically mounted tube was filled with stainless-steel turnings and surrounded by a 1200-watt Nichrome heater. The upper part of the tube contained a bed of Hopcalite catalyst 7/16 inch in diameter and 5 inches deep supported on a circular section of stainless-steel screen. This part of the tube was heated with a 600-watt Nichrome heater, and the whole assembly was insulated with a glass blanket and asbestos tape. The two heaters were independently controlled by variable voltage transformers which supplied the power. This arrangement permitted the gas to be preheated to the catalyst temperature and made it possible to operate the burner with only a small temperature differential across the catalyst bed. The temperatures of the gas entering and leaving the bed were measured by means of two Chromel-Alumel thermocouples connected to suitable meters.
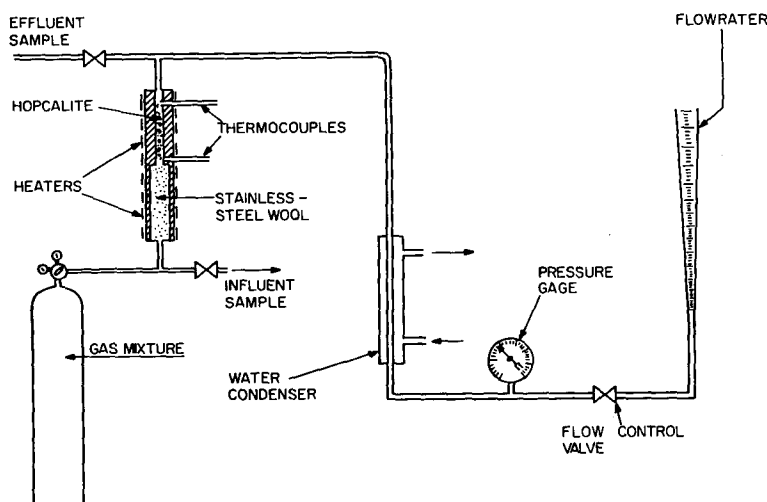

Fig. 3 – Laboratory catalytic burner

Stainless-steel lines and valves were provided to permit sampling of both burner influent and effluent and analysis by a gas chromatograph to determine how much CO was removed from the gas stream by the catalyst. The chromatograph used was a Beckman Model GC-2a with a catalytic reactor following the separation column to convert the CO to methane, for which the flame ionization detector has a high sensitivity.

The space velocity in operating CO/H_2 burners in submarines is 21,000 hr^{-1} or higher. To maintain a space velocity of 21,000 hr^{-1} at 300 psig, the laboratory reactor requires 3.2 cfm of gas as measured at atmospheric pressure and room temperature. At atmospheric pressure and the same space velocity, gas flow would be only 0.15 scfm.

The data for the removal of CO from gas mixtures by Hopcalite catalyst are summarized in Table 1. Compressed air containing 5 to 6 ppm CO was used to make blank runs and to confirm that the catalyst did oxidize the CO. At 600°F and with no Hopcalite in the burner, the chromatographic analyses showed that the CO passed through the burner without loss or holdup. With Hopcalite in the burner, all the 5 to 6 ppm of CO was removed from dry air under three different sets of operating conditions: room temperature and atmospheric pressure, room temperature and 300 psig, and 600°F and 300 psig. A space velocity of 21,000 hr^{-1} was used in all of these experiments.

Table 1
Catalytic Oxidation of CO at High Pressure

| Mixture | CO Conc. (ppm) | Flow Rate* | | Pressure (psig) | Temperature (°F) | | Time (hr) | Cum. Time (hr) | Cum. Flow (ft³) STP | % CO Removed | Catalyst Used |
		L/min	CFM		Influent	Effluent					
Compressed air	5-6	–	3.2	300	600	–	–	–	–	0	None
Compressed air	5-6	–	0.15	Atm	Room	Room	–	–	–	100	Hopcalite
Compressed air	5-6	–	3.2	300	Room	Room	–	–	–	100	Hopcalite
Compressed air	5-6	–	3.2	300	540-680	480-620	–	–	–	100	Hopcalite
1.7% O$_2$ in He	28	8.8	–	3	615	540	3.25	3.25	65.2	100	Hopcalite
1.7% O$_2$ in He	28	2.0	–	3	700	480	0.92	4.17	68.1	–	Hopcalite
1.7% O$_2$ in He	28	0.1	–	1-1/2	600	370	17.70	21.87	71.9	100	Hopcalite
1.7% O$_2$ in He	28	4.25	–	3	620	475	1.60	23.47	86.4	100	Hopcalite
1.7% O$_2$ in He	28	–	3.2	300	600	580	0.42	23.89	166.4	100	Hopcalite
1.7% O$_2$ in He	28	4.25	–	2-1/2	630	330	5.22	29.11	213	100	Hopcalite
1.7% O$_2$ in He	28	4.25	–	3	620	600	8.00	37.11	285	100	Hopcalite

*Volumes were calculated at 1 atmosphere and room temperature.

Following the preliminary runs with 5 to 6 ppm CO in air, a mixture of 28 ppm CO and 1.7% O$_2$ in helium was used. During continuous operation for about 24 hours at 1-1/2 to 3 psig pressure and 600°F, about 86 ft³ of the gas mixture was passed through the catalyst bed at flow rates varying from 0.1 liters per minute (500 hr^{-1}) to 8.8 liters per minute (44,000 hr^{-1}). The burner then was operated at full-scale conditions (300 psig, 600°F, and 21,000 hr^{-1}) for 25 minutes. After operating at the full-scale conditions, the burner then was operated at 3 psig, 600°F, and 21,000 hr^{-1} (4.25 liters per minute) for more than 13 hours. The last 8 hours of operation were timed after the burner had been allowed to cool down overnight and reheated the next day. During the cool period an atmosphere of the 28-ppm CO gas mixture was maintained in the system. The total operating time was 37 hours, during which time 285 ft³ of the 28-ppm CO mixture was passed through the bed. Frequent analyses were made during this period, and no CO was detected in the burner effluent.

The 285 ft³ of gas handled by the laboratory burner in 37 hours is equivalent to the volume it would handle in 89 minutes operating at 300 psig. On the basis of CO removal, 89 minutes of operation at 28 ppm CO is equivalent to 42 hours at 1 ppm CO, which is approximately the maximum concentration limit desired.

On the basis of these experimental results, a Hopcalite burner was built by the Mine Defense Laboratory for DSSP to be used in the SeaLab III program. This burner was designed to process 4 ft^3/min helium at the operating pressure and to be capable of processing double that volumetric flow rate provided only that the air pump be changed for another of suitably larger size. This burner as constructed could hold the CO concentration to 1 ppm even if the CO generation rate were 1.5 times that of SeaLab II. By using the higher capacity pump, the burner should handle 3 times the SeaLab II generation rate of CO.

Catalytic Combustion of Carbon Monoxide in the Presence of n-Decane, Paint Thinner, and R-12

A series of experiments was conducted to determine whether the presence of n-decane, NTU-4 (a paint thinner derived from petroleum distillate), or R-12 would affect the ability of Hopcalite to oxidize CO. The basic apparatus shown in Fig. 3 was modified for these experiments by using the 90-psig laboratory air line, rather than a high-pressure bottle, as a source of air. Also, lines and metering valves were added to the system to permit bleeding the gaseous contaminants (CO and R-12) into the main air stream. The air stream was contaminated with n-decane and NTU-4 by passing part of it through a bubbler containing the contaminant. One other change was the inclusion of a water bubbler with suitable valves in the system so that the air supplied to the burner could be humidified to different specified degrees.

The CO was analyzed by a Beckman Model GC-2a gas chromatograph as it was in the case of the high-pressure work discussed above. The n-decane and R-12 contaminants were analyzed by means of a second GC-2a chromatograph, while the paint thinner was analyzed by a NRL Total Hydrocarbon Analyzer.

A summary of the results of the experiments is presented in Table 2. All of the work was done at a space velocity of 21,000 hr^{-1}, with the Hopcalite at about 600°F, and the system under a pressure of about 3 psig. This pressure was used to provide a reasonable flow rate of air through the gas chromatographic sampling loop. Relative humidities were varied from about 4% to 95% and operating times of the experiments from 2.65 to 10.65 hours.

Table 2
Catalytic Oxidation of CO in the Presence of
Other Contaminants

Exp. No.	Duration (hours)	R.H. (%)	Conc. CO (ppm)		Conc. n-decane (ppm)		Conc. NTU-4 (ppm)		Conc. R-12 (ppm)	
			Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
71	10.65	4	6-8	0	15-90	525	–	–	–	–
71	2.65	50	6-8	0	135-155	10-20	–	–	–	–
72	6.30	50	4-6	0	–	–	15-125	2-10	–	–
72	7.40	50	5-12	0	–	–	30-95	2-10	–	–
73	6.33	4	0.5	0	–	–	–	–	135-175	135-175
78	7.05	95	0.1-0.5	0	–	–	–	–	85-115	85-115
79	8.07	95	20-22	0	–	–	–	–	95-110	95-110

The data show that none of the three contaminants interfered with the action of the Hopcalite sufficiently to prevent the complete oxidation of the CO. With a 6 to 8 ppm concentration of CO and 15 to 90 ppm concentration of n-decane in the burner influent at 4% R.H., all the CO and more than half of the n-decane were oxidized. With the same concentration of CO, higher concentrations of n-decane (135 to 155 ppm), and at higher humidity (50% R.H.), all of the CO and most of the n-decane were oxidized.

With 4 to 12 ppm of CO and 15 to 125 ppm of NTU-4 (paint thinner) in 50% R.H. air, the catalyst again oxidized all of the CO in addition to 80 to 90% of the paint thinner.

In the case of the R-12 contaminant present with CO, no appreciable amount of R-12 was oxidized by the catalyst, but all of the CO was oxidized. This was true under three different sets of conditions: low CO concentration (0.5 ppm) and low humidity (4% R.H.), low CO concentration (0.1 to 0.5 ppm) and high humidity (95% R.H.), and high CO concentration (20 to 22 ppm) and high humidity (95% R.H.).

Catalytic Combustion of Thiophene

Although it is known that sulfur compounds must be present in nuclear submarines, particularly in diesel fuels, the action of the CO/H_2 burner on this class of compounds has not previously been studied. For preliminary work on sulfur compounds in the CO/H_2 burner, thiophene (C_4H_4S) was chosen. Thiophenes are important constituents of petroleum products, sometimes accounting for 50% or more of the sulfur compounds found in the kerosene-boiling range.

The apparatus used for these studies employed a larger burner than that shown in Fig. 3. A 1-sq-in. bed of Hopcalite 5 inches deep was used with a 1-ft^3/min airflow rate to give a space velocity of 21,000 hr^{-1}. All the experiments were made with the influent humidity at 50 to 60% R.H., the catalyst bed temperature at approximately 600°F, and the system pressure at about 3 psig. Eight experiments with thiophene were made in which the duration varied from a little less than 4 hours to almost 25 hours, and the concentration of thiophene in the burner influent varied from about 5 to 145 ppm. The thiophene was added to the air stream by means of a bubbler or diffuser.

A summary of the experimental results is shown in Table 3. Seven of the experiments (No. 122 to 128) were made using a single catalyst bed, while the eighth (No. 137) used another bed which had not been exposed previously to thiophene. With two exceptions, the influent concentrations of thiophene were in the 40 to 100 ppm range and the proportion of the influent thiophene oxidized was about 40 to 50%. The proportion of the thiophene oxidized is taken as that measured after a few hours of operation. The proportion oxidized early in the run is generally higher than the 40 to 50% range. In one of the exceptions (exp. 124), a very low concentration of thiophene (about 5 ppm except at the start) was present in the burner influent and a higher proportion (72%) was oxidized. In the other exception (exp. 127), the influent contained a higher concentration of thiophene (130 to 145 ppm) than was present in the other experiments and a lower proportion (35%) was oxidized.

As air contaminated with thiophene was passed into the burner, the burner effluent was analyzed for sulfur dioxide (SO_2) and hydrogen sulfide (H_2S) by means of detector tubes. Also, the burner exhaust was analyzed for strong acids by means of the NRL acid detector paper. No SO_2 or H_2S was detected, but in some cases a trace of acid (0.2 to 1 ppm) appeared to be present.

Further work with thiophene and other sulfur compounds is planned because of their potential importance in contaminated atmospheres.

Table 3
Catalytic Oxidation of Thiophene

Exp. No.	Duration (hr)	Influent Conc. (ppm)	Effluent Conc. (ppm)	Amount of Oxidation (%)	
				At Start*	At End
122	4.93	55-115	10-50	89	50
123	6.18	15-110	5-55	73	48
124	6.61	5-6	1-3	74	72
125	3.68	65-105	35-55	48	48
126	6.02	60-75	20-45	60	42
127	7.27	130-145	70-100	43	35
128	6.91	35-45	20-25	41	43
137	24.91	60-70	20-30	72	52

*After the influent concentration has been adjusted to approximately a constant value, usually about 1 hour after the start of the experiment.

Summary and Conclusions

It was found in the laboratory that Hopcalite catalyst at 600°F completely removed CO from a simulated SeaLab atmosphere (1.7% O_2 -98.3% He) at pressures up to 300 psig. Based on experimental results and the experience of SeaLab II, a catalytic burner was built for SeaLab III. This burner was designed to process 4 ft^3/min of atmosphere, or alternatively 8 ft^3/min when modified by the substitution of a larger air pump.

Hopcalite at 600°F effectively oxidized CO in the presence of n-decane, paint thinner (NTU-4), or R-12 in relatively large concentrations (to 150 ppm).

With 40 to 100 ppm thiophene in the burner influent, Hopcalite at 600°F oxidized 40 to 50% of the input. Higher percentages of thiophene were oxidized early in a run, particularly by fresh catalyst. The proportion oxidized appeared to vary with the concentration of thiophene in the influent. No SO_2 or H_2S was detected in the effluent from a catalytic burner oxidizing thiophene. However, a trace of acid was detected in some instances.

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Chapter 3

THE NRL TOTAL HYDROCARBON ANALYZER

Harold G. Eaton

INTRODUCTION

As reported previously (1,2), the atmosphere inside a nuclear-powered submarine can become contaminated during an extended submergence. These contaminants are contributed by a wide variety of sources, including human effluents, cigarette smoke, refrigerant leakages, paints, cooking, diesel fuel, and degreasing solvents. The principal means of removing these trace contaminants from the atmosphere in a sealed nuclear submarine are oxidation by the CO/H_2 burner and adsorption on activated charcoal. In addition, control of contamination sources is an important preventive measure against buildup of such materials.

The Navy Toxicology Unit has recommended that concentrations of total hydrocarbons be set at 40 mg/m^3. Limits have also been recommended for other trace contaminants. To adhere to these recommended concentration limits, the concentrations of the contaminants in submarines must be measured. By monitoring these concentrations, it would be possible to check the effectiveness of removal systems and to control the sources of the contaminants, at least in many cases.

In response to this need, a program has been carried out at NRL to develop an instrument to monitor the trace organic contaminants in nuclear submarines. This instrument has been named the Total Hydrocarbon Analyzer, THA, because the bulk of the contaminants are hydrocarbons or substituted hydrocarbons.

THE TOTAL HYDROCARBON ANALYZER

The operation and development of the THA have been reviewed previously (3,4). However, for completeness, this method of analysis will be described briefly. The THA, as shown in Fig. 4, is a gas chromatograph (GC), using as its detection sensor a hydrogen flame ionization detector (FID). The data from the analyzer are presented on a 1-mv strip chart recorder.

As shown in the schematic flow diagram in Fig. 5, compressed air, taken from the compressed air banks aboard the submarine, flows first into a catalytic air purifier, then through a LiOH column. This tandem arrangement presents purified air to the THA. When this air enters into the THA, it is separated into two parts—the bottom portion serves as the combustion air to support the FID, while the other portion serves as the carrier air to push the injected sample through the separation column into the detector. At present, the source of hydrogen to support the flame in the FID is from a compressed cylinder.

The THA has the capability of operating in two modes. First, an injected sample can be chromatographed in the conventional manner by allowing the sample to pass through the labeled four-way valve along the solid path, through the separation column back to
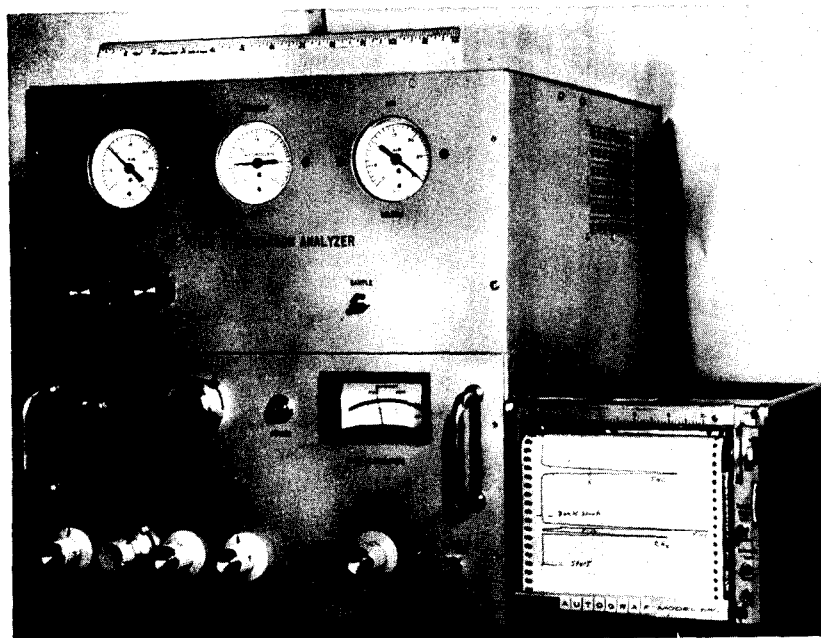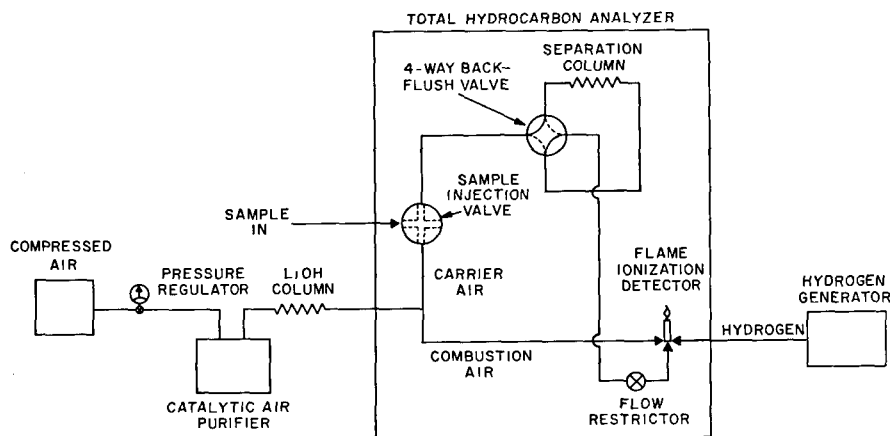
Fig. 4 - Total Hydrocarbon Analyzer

Fig. 5 - Schematic flow diagram of the Total
Hydrocarbon Analyzer

the four-way valve, and then into the FID. Operating in this manner, the components in
the injected sample are eluted from the column and are detected by the FID depending
on the volatilities of the individual components—the more volatile components being eluted
first.

However, it has been reported that over 200 individual components have been detected
in nuclear submarines (5), and these components differ widely in volatility and concentra-
tions, making it impractical to detect all of them by the above mode of operation. Hence
a back-flush mode is used. Following an injected sample again through the column, the
more volatile components, CH_4, R-12, and R-114, which are normally higher in concentration

in comparison to the other hydrocarbons, are allowed to elute from the column as before. Then the flow through the four-way valve is reversed, by which action the back-flush is actuated to regroup all the components remaining on the column into one lumped peak. This is pictured in the flow diagram by following the path of the dashed lines through the four-way valve, to the opposite end of the column, four-way valve, and then into the FID. The presentation obtained in this manner represents the total hydrocarbons present in the atmosphere, with the exception of the volatile components which passed through the detector earlier.

The two modes of operation discussed above are shown chromatographically in Figs. 6 and 7. Figure 6 represents the elution of many individual contaminants found in the atmosphere of nuclear submarines. At approximately 55 minutes the flow through the separation column is reversed or back-flushed, and the remaining contaminants not previously eluted are regrouped into one measurable peak and are eluted at approximately 53 minutes after the back-flush is actuated.
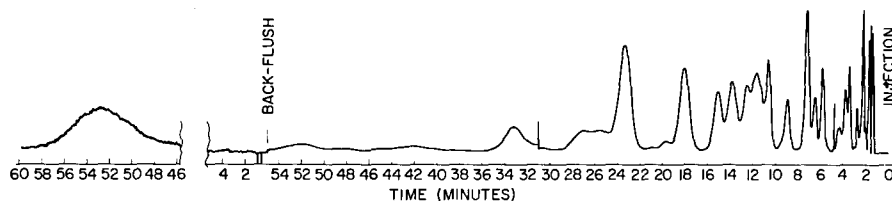

Fig. 6 – Delayed back-flush mode
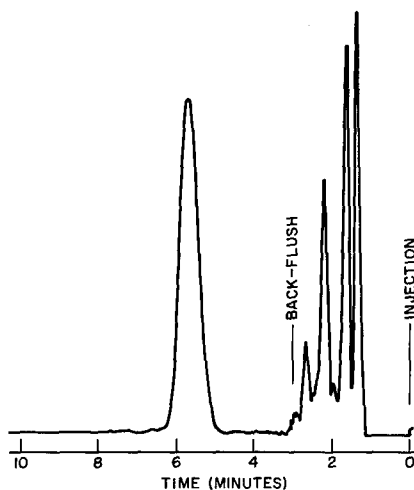

Fig. 7 – Back-flush mode

Figure 7 represents the expected normal operation of the THA unit whereby the back-flush is actuated just after the elution of the volatile contaminants, such as methane, to get a composite peak which represents the total hydrocarbons present in the atmosphere. Operating in this manner the total hydrocarbons are recorded within 7 minutes.

COMPONENT DEVELOPMENT

The development of the THA has been completed. The separation column which was finally recommended was optimized to give the desired separation of the individual contaminants of interest as shown in Fig. 6 and to give a total hydrocarbon presentation as shown in Fig. 7. This column is a 10% Dow Corning Silicone 200 liquid phase on Chromosorb G, 45/60 mesh packed into an 8-foot length of 1/4-inch O.D. stainless-steel tube. The column is operated at a temperature of approximately 55°C.

As reported previously (4), it was recommended that the catalytic air purifier used to purify the air from the compressed air banks be operated at a lower temperature than 600°C. This was accomplished by using 1/16-inch pellets instead of 1/8-inch pellets of 0.5% palladium on alumina. The operating temperature now recommended is approximately 450°C.

As stated earlier in this report, bottled hydrogen is presently the source of hydrogen for the FID. This laboratory has recently evaluated an electrolytic hydrogen generator built by a commercial manufacturer for use aboard the submarine. With minor changes which were recommended to NavSec and the manufacturer, it is quite possible that a generator so modified might be used as a adjunct to the THA. This would eliminate the problem of supplying bottled hydrogen gas to the boats.

COMMERCIAL PROCUREMENT OF THE TOTAL HYDROCARBON ANALYZER

In the course of developing the THA at NRL, several complete instruments were fabricated and were used on nuclear submarines by NRL personnel. Also on several cruises the THA was operated satisfactorily by ship personnel in the absence of laboratory personnel. Based on the excellent performance of these laboratory-built THA units, the Navy decided to provide an instrument for each nuclear submarine. NRL cooperated closely with NavSec in providing technical assistance in preparation for commercial procurement.

Because of the desire to provide the THA for each submarine as soon as possible, NavSec contracted with three commercial firms to fabricate the shipboard units. Some deliveries of completed instruments have already been made, and it is expected that shipboard installations will begin in 1970.

UNCLASSIFIED

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Chapter 4

GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC
ANALYSIS OF THE SUBMARINE ATMOSPHERE

R. A. Saunders

INTRODUCTION

Chromatographic measurements made of samples taken during the Habitability Cruise of the USS Nautilus in 1956 established the belief, generally held since that time, that 300 or 400 trace organic contaminants exist in the typical submarine atmosphere. Obviously, there are many sources of contaminants in a submarine, but probably the one which contributes the greatest number of individual compounds to the atmosphere is cigarette smoking. A recent publication (1) gave the total constituents identified to date in tobacco smoke as 700, and further mentioned additional chromatographic data indicating the presence of many times that number which have not been identified. The point is, there is evidence for 12,000 components in cigarette smoke (1), and it follows that there is undoubtedly an even greater number of contaminants in a submarine atmosphere! The analysis of such a complicated mixture is certainly not simple or straightforward even with the best modern instrumentation.

ANALYTICAL DIFFICULTIES

Many of these contaminants are liquid or solid particulates rather than vapors and are not recovered from a charcoal sampler. However, several hundred components can be recovered which originally existed in the atmosphere in the gaseous state. But a typical chromatogram of this mixture shows only 75 to 200 peaks, depending on the type of chromatographic column used for the separation, and many of this number will be incompletely resolved. Since there are many more components in the mixture than there are peaks on the chromatogram, it is obvious that some of the peaks will represent more than a single compound - some, perhaps, as many as 10 or more.

When a quantity of the mixture recovered from a submarine charcoal is injected onto one of the better chromatographic columns and the effluent from the column passed into a rapid scanning mass spectrometer, the mass spectrum of the material represented by some of the chromatographic peaks will be attributable to one or two compounds and will be relatively easy to interpret. However, the mass spectrum of the material eluted together as a mixture of 8 to 12 components will be quite complex and difficult to interpret even though the mixture is represented by a single chromatographic peak. If the components in question are representative of several different chemical classes, a specific identification for several, and perhaps all, of the components can be established from the single mass spectrum. However, if most of the components represented by the single chromatographic peak embrace only one chemical class, e.g., aliphatic hydrocarbons, as is most often the case, a single mass spectrum would probably suffice only to characterize the compounds as such, and few, if any, specific identifications could be made.

Ordinarily, a mass spectroscopist skilled in the analysis of hydrocarbon mixtures could unravel the spectrum of a mixture of several similar hydrocarbons and identify each constituent with a fair degree of certainty. His ability to do this, among other things, is based on the congruency of his spectra and the available spectra of pure reference compounds, assuming all the spectra were recorded at standardized operating conditions and at constant pressure. But this is not the case with the spectra obtained with a rapid scanning mass spectrometer of fractions eluted from a high-resolution chromatographic column, because, in this instance, the pressure of the material in the inlet system of the mass spectrometer varies from zero to maximum and back to zero in the 2 or 3 seconds time required for the material to elute from the column. Unfortunately, this is only a slightly longer time period than that required to record the mass spectrum, with the result that the intensity of the mass peaks varies, from one end of the spectrum to the other, upwards or downwards or both, relative to the intensity of the same spectrum recorded at constant pressure, depending on whether the mass spectrum is recorded on the leading edge, the trailing edge, or near the maximum of the chromatographic peak. This circumstance precludes the possibility, in many cases, of obtaining even approximate correspondence between the mass peak intensity contributions of a suspected component in a rapidly scanned spectrum of a mixture - represented by a single chromatographic peak - and the mass peak intensities of the reference spectrum of the appropriate pure compound. This effect is illustrated in Fig. 8. The changed intensities in this figure with respect to the reference spectrum do not portray actual experimental recordings but are simulations which were accomplished photographically for illustrative purposes. The differences may appear slight, but they are enough to remove the certainty from some identifications and wholly prevent others.

Another happenstance which adds to the difficulty of using a single mass spectrum for the specific identification of all of the components of a mixture of compounds that might elute from a GC column at essentially the same time is the fact that the concentration of the various components of the mixture may differ by one to two orders of magnitude. The spectral contribution of the components present at low relative concentrations may be all but obscured by that of the more concentrated components.

METHOD OF SOLUTION

One way of circumventing these difficulties is to collect the material eluted at a given time from the chromatographic column, when such material is thought to represent a mixture of components, and reinject it onto a second column having a different stationary liquid phase, one that is more advantageous for the separation of that particular type of mixture. The proper choice of a second column would, ideally, allow complete resolution of the mixture and present a chromatogram with a sharply separated peak for each component of the mixture. As these components elute from the column a "clean" mass spectrum of each one would be recorded, from which an unambiguous identification could be made. Since this ideal will not always be realized, possibly a repetition of the procedure using a third column would be necessary for particularly troublesome mixtures.

There have been many techniques developed for collecting fractions from GC columns, including high-resolution, low-capacity columns, but few of them are convenient for reinjecting the collected fraction onto another column. Figures 9 through 11 depict a fraction collector designed at NRL for the particular type of chromatographic equipment available and for the problem outlined here. The device was designed for collecting material eluted from high-resolution, packed and open tubular columns of low capacity, and for reinjecting the collected fraction back onto other similar columns. The entire system, with the exception of the collection traps, is heated to prevent condensation.
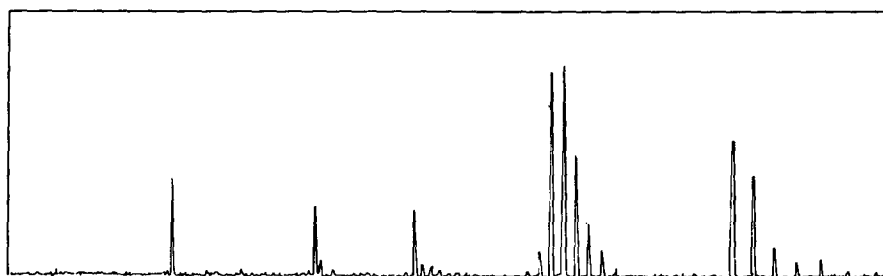
(a)
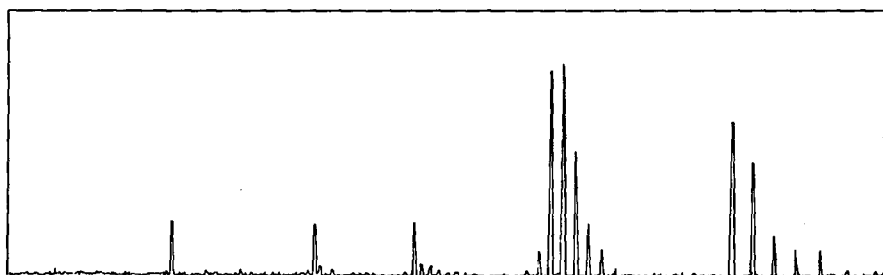
(b)

Fig. 8 - Simulated rapid scan mass spectra. The spectra represent
a sharply resolved component eluted from a high-resolution column
and are shown as they might appear if scanned at (a) the leading
edge, (b) the trailing edge, and (c) near the maximum of the chro-
matographic peak. The spectrum at (d) was recorded at constant
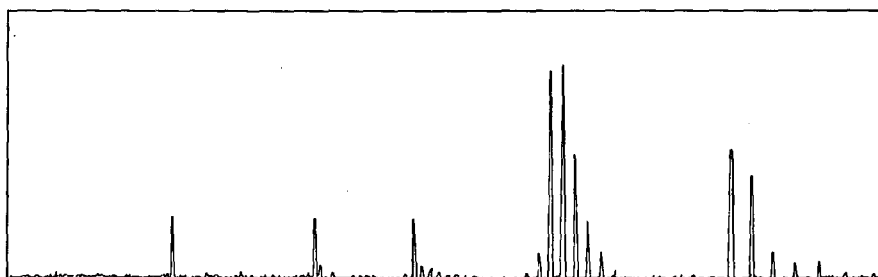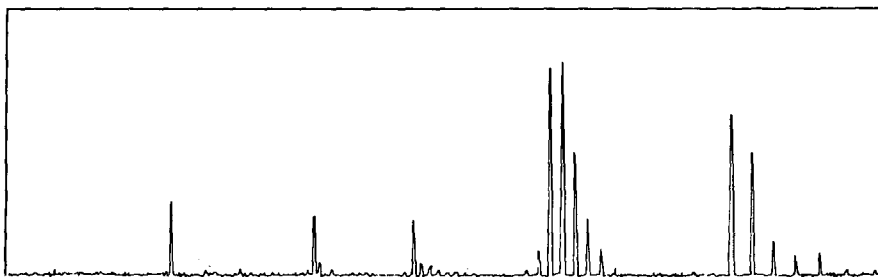pressure.   Continued-

(c)

(d)

Fig. 8 (Continued) - Simulated rapid scan mass spectra. The spectra represent a sharply resolved component eluted from a high-resolution column and are shown as they might appear if scanned at (a) the leading edge, (b) the trailing edge, and (c) near the maximum of the chromatographic peak. The spectrum at (d) was recorded at constant pressure.
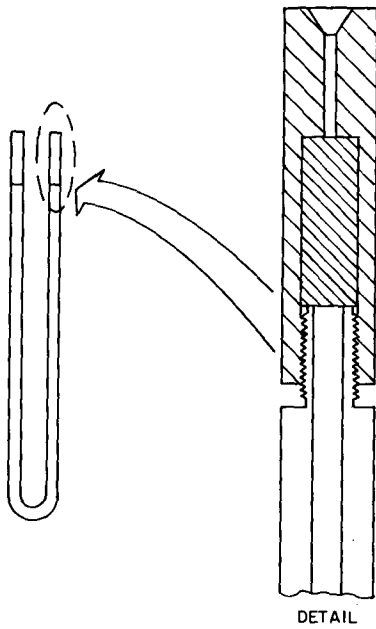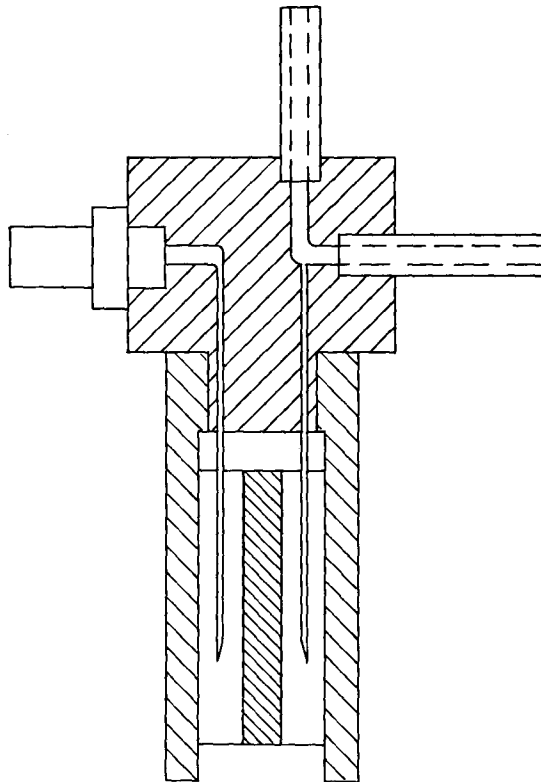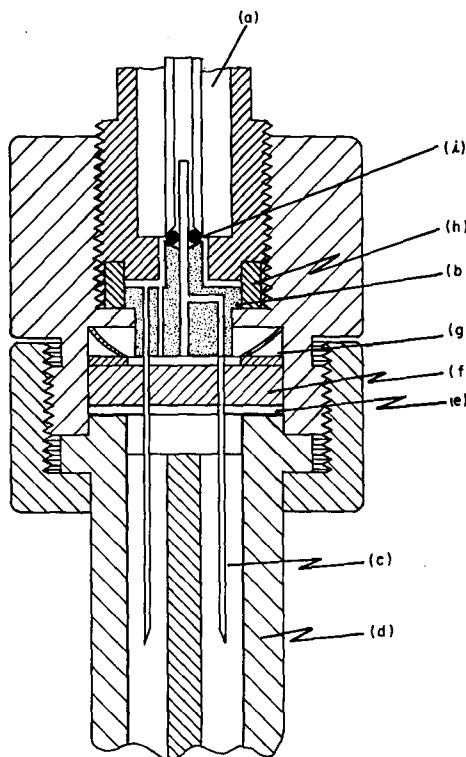
Fig. 9 - Collection trap

DETAIL

Fig. 10 - Collection station

Fig. 11 - Reinjection station

The column effluent is split between the detector and the collecting device. The splitter, the connecting tubing to the collector, and the passageways through the collector station have the same, or smaller, internal diameter as the column to avoid disruption of a smooth flow of the effluent stream and a resultant lessening of the resolution previously afforded by the column.

The collection traps are U-shaped pieces of 1/8-inch O.D. stainless-steel tubing, 3/8 inch wide and 5 inches long overall. The open ends are terminated, as shown in Fig. 9, with removable fittings containing replaceable silicone rubber septums. The end pieces further serve as guides to direct accurately a pair of hypodermic needles in the collecting or reinjection station through the center of the rubber septums. The traps can be purged with dry helium just before use.

To collect a fraction the trap is dipped in a flask of liquid nitrogen associated with the collection station, the ends are inserted into guides on the collecting station (Fig. 10), and the trap is slid upward, where the hypodermic needles on the collecting station pierce the septums. During the short time the needle tips are in the rubber, the effluent stream is vented to the atmosphere through the side arm shown. When the trap is in the proper position, this opening is closed with a finger and the column effluent passes through the trap, the bottom third of which is immersed in liquid nitrogen. Organic material in the effluent remains in the trap while the carrier gas vents to the atmosphere. When the fraction has eluted, the trap is removed and replaced with another. Traps can be removed and replaced in just a few seconds. The lower part of the trap can be packed with an inert solid column packing material, if desired, as an aid to collection efficiency. There is no need to cool the traps after the fraction has once been collected.

The reinjection station, Fig. 11, screws onto the regular injection part of the chromatograph in place of the normal septum fitting. The flow of carrier gas through the

instrument to the column is as follows: through the annular space surrounding the input liner (a) and through the channels in the needle support (b) to the column input liner. The channels through the hypodermic needles (c) are blocked at this point, being half inserted into the rubber septums of a collection trap, which has not yet been fully seated. The trap is positioned in a holder (d), which is heated for the full length of the trap and which accurately guides it onto the needles. When injection is desired, the trap is seated firmly, the needles fully penetrate the septums, and the top of the trap forces a metal plate (e) and a rubber seal (f) against the bottom of the needle support, sealing the gas passageways. Carrier gas flow is now through the needles and trap, flushing the collected fraction onto the column. When the trap is removed, the rubber seal is returned to its original position by a spring washer (g). Other gastight seals are provided by a Teflon gasket (h) and an O ring (i).

FUTURE PLANS

A gas chromatograph linked to the input of an Atlas CH4 rapid-scanning mass spectrometer, a combination which has been described previously (2,3), and the auxiliary techniques described above will be used to identify as many of the vapor-state contaminants in the nuclear submarine atmosphere as possible. Information concerning the concentration of the various contaminants of interest will be derived from the chromatographic data.

An analysis of the atmospheric contaminant profile of a normally operating submarine is necessary and desirable for a number of reasons. It is an obvious prerequisite for toxicological studies of the short- and long-range effects of the various individual contaminants on the health and performance of submarine personnel. Such an analysis would be helpful additionally in explaining the cause of equipment damage or failure, when such is attributable to atmospheric conditions. A background analysis of a normal submarine atmosphere would also be a tremendous aid in establishing the identity and source of a previously unencountered toxicant during or following any troublesome atmospheric incident. And finally, more detailed knowledge of the organic content of a normal atmosphere would contribute significantly to problems involving design and regulation of submarine atmosphere analytical and control equipment. Work on the general analysis of a submarine atmosphere is now in progress.

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Chapter 5

CO$_2$ ABSORPTION PROPERTIES OF SOME NEW AMINES

Paul R. Gustafson

INTRODUCTION

Due to certain undesirable properties of monoethanolamine (MEA), the regenerative absorbent used in CO$_2$ scrubbers aboard nuclear submarines, a number of CO$_2$-absorbing chemicals have been studied as potential replacements. The system MEA-DMAC (N,N-dimethylacetamide) was discussed in the previous annual report (1). The following systems are now reported with regard to CO$_2$ absorption and stripping:

amine-DMAC-H$_2$O

amine-Sulfolane (tetrahydrothiophene 1,1-dioxide)-H$_2$O

amine-N-methyl-2-pyrrolidinone (NMP)-H$_2$O

MEA-hexamethylphosphorotriamide (HMPA)-H$_2$O

amine-dimethylformamide (DMF)-H$_2$O

amine-tetramethylurea (TMU)-H$_2$O.

The amines were monoethanolamine (MEA), 2-(2-aminoethoxy) ethanol (DGA), and 3-amino-1-propanol (MPA). Another amine (not commercially available), 3-(methylsulfonyl)-1-propylamine, was synthesized and will be discussed later in this chapter.

CO$_2$ SOLVENTS

The addition of a CO$_2$ solvent, such as TMU, Sulfolane (S), or NMP, to an amine-H$_2$O composition can be beneficial, not only with regard to CO$_2$ absorption and stripping but also with regard to aiding in the reduction of foam and aerosol fog.

Three organic CO$_2$ solvents of potential submarine use, Sulfolane (2), NMP (3), and TMU (4), with their boiling points, freezing points, flash points, and reported toxicities, are listed in Table 4. These solvents possess good thermal stability, noncorrosiveness, and a resistance to hydrolytic cleavage. Hexamethylphosphorotriamide, $[(CH_3)_2N]_3PO$, may also be suitable if its odor can be removed; however, the possibility of the rapid absorption of spilled liquid through the skin is an undesirable property of this compound.

CO$_2$ ABSORPTION RATES OF AQUEOUS AND TRILIQUID AMINES

Figure 12 compares the absorption rates of 4N MPA, 4N MEA, and 6.5N DGA (this was the concentration recommended by the manufacturer) aqueous solutions. MPA is slightly more efficient, and DGA significantly less efficient, with respect to the rate of CO$_2$ absorption, than MEA. After 1 hour, DGA had sorbed 26 volumes of CO$_2$, corrected

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Table 4
Organic CO_2 Solvents of Potential Suitability

Substance	Boiling Point (°C)	Freezing Point (°C)	Flash Point (open cup) (°C)	Oral Toxicity LD_{50} g/kg Rats
Sulfolane $CH_2CH_2CH_2CH_2SO_2$	285	27.6	176.7	0.5 - 5
NMP $CH_3N(CH_2)_3CO$	202	-24.4	95	7
TMU $[(CH_3)_2N]_2CO$	176.5	-1	148	0.8
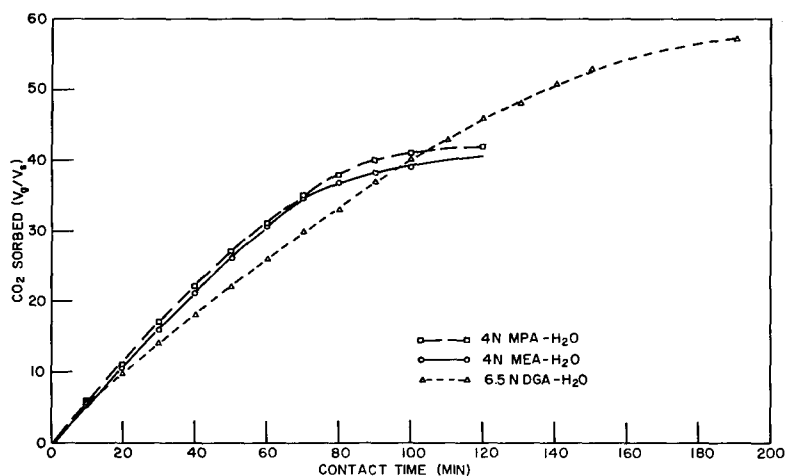
Fig. 12 - CO_2 absorption rate of various amines in H_2O, using a flow rate of 3.3 l/min of 1% CO_2 in air at 1 atm, 88°F, and 100% R.H.

to STP, per volume of liquid (hereafter termed V_g/V_s), while MEA sorbed 30 V_g/V_s units, or about 15% more. After 100 minutes, the CO_2 sorbed is approximately the same for all three amines. The overall CO_2 capacity of the 6.5N DGA solution is nearly 1.5 times that of the 4N amines, as one would expect.

The absorption rates of MEA, DGA, and MPA are improved when an organic solvent, such as TMU or NMP, is added (Figs. 13 and 14). With MEA (Fig. 13), both organic solvents increased the CO_2 absorption efficiency. The rate remained high relative to aqueous MEA with TMU as the additive; but with NMP, the efficiency fell below aqueous MEA after 60 minutes. This is not too significant, since 75% of the amine's CO_2 capacity was reached at this point.

Both TMU and NMP increased the absorption efficiency of MPA about 10%, but at the expense of lower CO_2 capacity. The capacity of the triliquid MPA solution was 49 V_g/V_s, compared with 54 for the aqueous 5N MPA solution (Fig. 14).
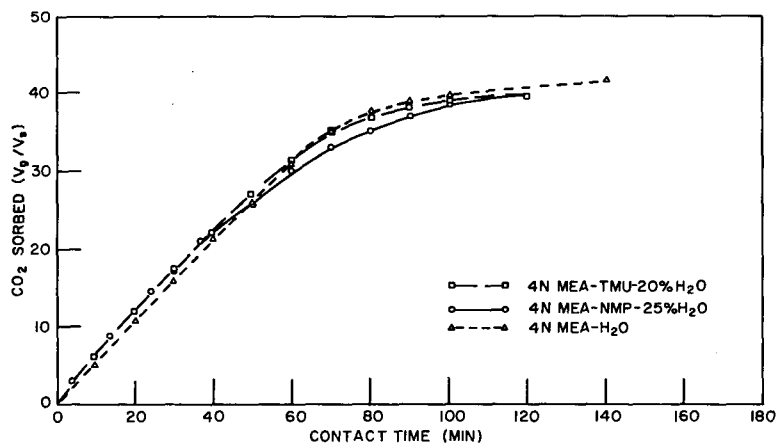
Fig. 13 - CO_2 absorption rates of MEA in organic solvent-H_2O mixtures, using a flow rate of 3.3 1/min of 1% CO_2 in air at 1 atm, 88°F, and 100% R.H.
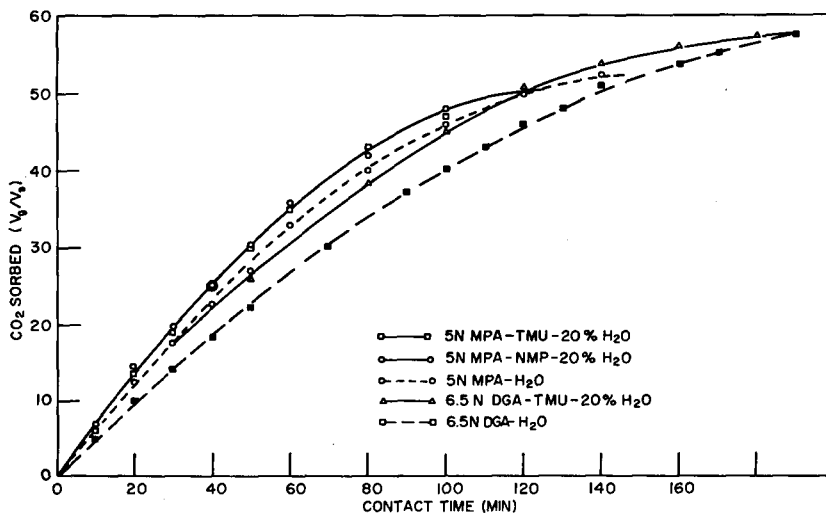
Fig. 14 - CO_2 absorption rate and capacity of MPA and DGA in organic CO_2 solvents, using a flow rate of 3.3 1/min of 1% CO_2 in air at 1 atm, 88°F, and 100% R.H.

TMU makes a significant improvement on the CO_2 absorption rate of aqueous DGA. At 60 minutes, the difference is approximately 5 V_g/V_s units; this amounts to about a 20% gain in efficiency for the DGA-TMU-H_2O mixture. In contrast to the 4N amines MEA and MPA, the addition of TMU to aqueous DGA does not lower the total CO_2 capacity.

Table 5 compares the CO_2 absorption rates of amine-Sulfolane-H_2O compositions with those of the corresponding amine-H_2O mixtures. Sulfolane increases the CO_2 absorption rate of DGA by 10%. However, the rate drops after 70 minutes. The CO_2 sorbed at this point is 65% of the equilibrium loading for the conditions of the test. After 110 minutes (90% equilibrium CO_2 loading for 5.4N DGA-Sulfolane-H_2O), the CO_2 absorption rate of the aqueous 6.5N DGA solution exceeds that of the 5.4N DGA-Sulfolane-H_2O composition. In both cases, 5.4N DGA-Sulfolane-H_2O and aqueous 6.5N DGA, the equilibrium loading was 86% of the theoretical carbonate or carbamate value of the corresponding amine

Table 5
Absorption Rate of Various Amines in Sulfolane

Sample	Absorption Rate (V_g/V_s) at Various Time Intervals (minutes)														
	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150
5.4N DGA-S-H_2O 20%	6	11	16	20	25	29	32	35	38	41	43	45	47	48	–
6.5N DGA-H_2O-35%	5	10	14	18	22	26	30	33	37	40	43	46	48	51	53
4N MPA-S-H_2O 20%	6	12	17	22	26	30	33	36	37	39	–	40	–	–	–
4N MPA-H_2O	6	11	17	22	27	31	35	38	40	41	–	42	–	–	–
4N MEA-H_2O (low foam)	5	10	15	20	25	30	34	37	38	39	–	–	–	–	–
4N MEA-H_2O (high foam)	6	11	17	23	28	33	37	40	42	43	–	–	–	–	–

Note: The conditions were a flow rate of 3.3 l/min of 1% CO_2 in air at 1 atm and 88°F, using a 50-ml sample.

normality. This is in contrast to MEA and MPA, in which the equilibrium loading was 90 to 95% of the corresponding aqueous solution for the same normality.

The MPA-Sulfolane-H_2O compositions absorb CO_2 nearly as efficiently as aqueous MPA of the same normality and more efficiently than either aqueous MEA or MPA under the same foam conditions.

Table 6 shows the average CO_2 (rounded off to the nearest 0.05%) in the effluent gas stream at various CO_2 loadings for both aqueous and triliquid amine solutions. The range of the foam column height is also listed. Triliquid solutions (in Table 6) show little tendency toward foaming under the conditions of the test. The foam column height of the triliquids does not vary significantly, although the bubble size may change, whereas with aqueous MEA or MPA, foaming tended to increase with contact time. Nonaqueous amine-organic solvent and triliquid amine solutions of reduced H_2O content foamed more than the triliquid compositions of Table 6 but less than the corresponding H_2O-amine mixtures. The 25% H_2O compositions, in particular, foamed the least.

The amides, dimethylacetamide and dimethylformamide, improved the absorption rates of the three amines under investigation to a greater extent than did TMU, NMP, and Sulfolane. Sulfolane was more effective with DGA than with the other amines. Another advantage of DGA-Sulfolane over MEA-Sulfolane or MPA-Sulfolane is the lack of phase separation of the carbonated amine. Carbonated DGA is soluble in Sulfolane. A possible explanation may be the lower Sulfolane concentration (30%) in the DGA composition compared with 55 to 58% (by volume) Sulfolane in the MPA and MEA mixtures.

The greater effectiveness of DMAC, DMF, and, to a lesser degree, TMU may be due to the

$$CH_3C-N\!<, \quad HC-N\!<, \quad and >\!N-C-N\!<$$
(with O atoms double-bonded above each carbonyl carbon)
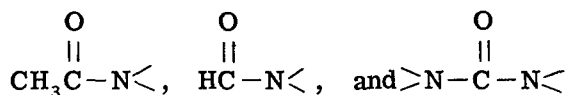
groups. Compounds containing one of the above groups, in general, possess a relatively high solubility for CO_2 compared with the solubility of CO_2 in water (5).

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Table 6

Percent CO_2 in the Effluent vs Amine-CO_2 Loadings

Sample	Foam Column Height Range (inches)	CO_2 in the Effluent (%) at Various Amine-CO_2 Loadings (V_g/V_s)						
		0	10	20	30	37	40	50
4N MEA-H_2O	1 - 10	0.25	0.25	0.25	0.30	0.55	0.80	
4N MEA-H_2O	3 - 10	0.15	0.10	0.10	0.30	0.45	0.80	
4N MEA-DMAC-H_2O (25%)	1/2 - 1	0.10	0.10	0.20	0.35	0.60	0.75	
4N MEA-NMP-H_2O (25%)	1/2 - 1	0.10	0.15	0.25	0.45	0.75	1.00	
4N MEA-TMU-H_2O (20%)	1/2 - 1	0.05	0.10	0.20	0.40	0.70	1.00	
4N MPA-H_2O	3 - 10	0.15	0.15	0.20	0.30	0.50	0.60	
5N MPA-H_2O	3 - 10	0.10	0.10	0.15	0.30	0.40	0.45	0.65
5N MPA-NMP-H_2O (20%)	1/2 - 1	0.05	0.05	0.15	0.30	0.40	0.50	1.00
5N MPA-TMU-H_2O (20%)	1/2 - 1	0.05	0.05	0.15	0.30	0.40	0.45	1.00
4 MPA-Sulfolane-H_2O (20%)	1/2 - 1	0.10	0.10	0.25	0.45	0.45	0.75	1.00
6.5N DGA-H_2O	1/2 - 1	0.20	0.30	0.35	0.45	0.50	0.50	0.65
5.8N DGA-DMF-H_2O (20%)	1/2 - 1	0.10	0.10	0.20	0.30	0.35	0.40	0.65
5.4N DGA-NMP-H_2O (25%)	1/2 - 1	0.20	0.20	0.30	0.40	0.50	0.55	1.00
6.5N DGA-TMU-H_2O (20%)	1/2 - 1	0.10	0.15	0.25	0.35	0.40	0.45	0.60
5.4N DGA-Sulfolane-H_2O (20%)	1/2 - 1	0.15	0.20	0.30	0.40	0.50	0.60	1.00

Note: The conditions were a flow rate of 3.3 l/min of 1% CO_2 in air at 88°C and 100% R.H., using a 50-ml sample.

STRIPPING

Of great importance is not only effective absorption but also regeneration. The triliquid solutions discussed in the preceding section not only absorbed CO_2 more efficiently than their aqueous amine counterparts but also, when heated, evolved larger amounts of their sorbed CO_2. This desirable effect varies inversely with the H_2O content, provided the solution's H_2O is not furnishing the only source of steam for purging. Thus, in Fig. 15, anhydrous 4N MEA-DMAC was almost completely regenerated in 120 minutes, while with aqueous 4N MEA, regeneration was not even 50% at the same conditions.

However, if steam is to be the sole component of the purge gas, H_2O must be present in the system (Fig. 16). When the purge gas (air) was decreased from 3 l/min to 0.6 l/min, the stripping efficiency of the anhydrous MEA-DMAC mixture drops considerably below that of aqueous MEA.

The stripping efficiency of the MEA-DMAC-H_2O solution also decreased (purge gas 0.6 l/min) but not to the same extent as the anhydrous solution. After 180 minutes, the stripping rate exceeded that of aqueous MEA. With aqueous MEA, the stripping rate remained relatively constant at purge gas flows varying from 0.6 to 3 l/min.

As shown in Fig. 17, organic solvents, such as DMF or NMP, did not improve the stripping efficiency of aqueous DGA but did result in lower levels of retained CO_2. Lower values of retained CO_2 are important, because they help to maintain a high CO_2 absorption rate in the next cycle.

Table 7 lists the stripping results of various amine compositions (MEA, MPA, and DGA), organic solvent (NMP, DMAC, DMF, and TMU), and H_2O. DMF and DMAC were the most efficient, followed by TMU and NMP in the order listed. The value of 39.3
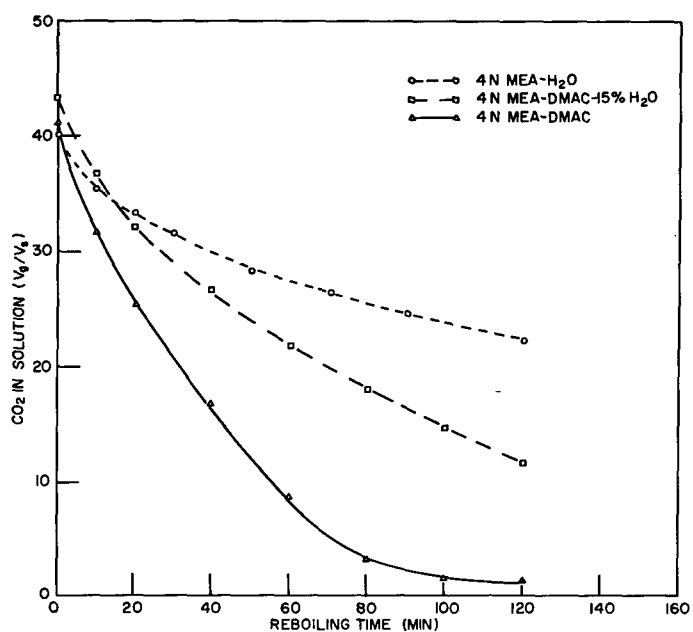
Fig. 15 - Stripping properties of MEA-DMAC-
H_2O mixtures, using an air purge over the liquid
surface at 3 l/min. The samples were in a 100 °C
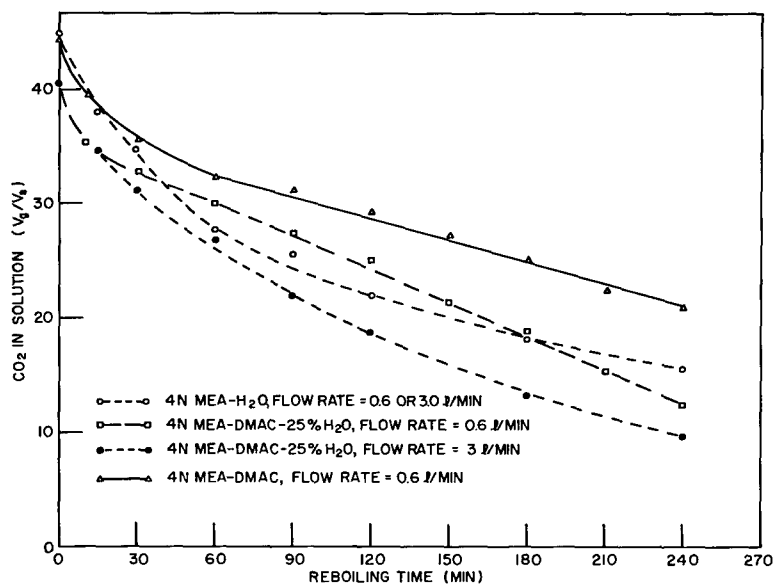H_2O bath at 1 atm.

Fig. 16 - Stripping properties vs purge gas flow rate
over the surface of the liquid. The sample tempera-
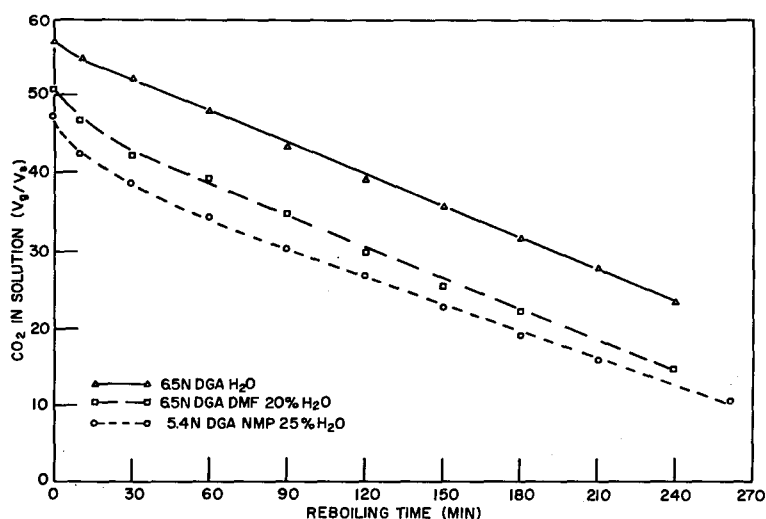ture was 92°C, and the pressure was 1 atm.

Fig. 17 - Stripping properties of aqueous DGA vs DGA in organic solvents. The sample temperature was 92°C, and the pressure was 1 atm.

Table 7
Stripping Results of Various Amine-Solvent Compositions

Reboiling Time (minutes)	Stripping Rate (V_g/V_s) of Various Amine-Solvent Compositions									
	4N MEA				5N MPA				6.5N DGA	
	NMP-25% H_2O	DMAC-25% H_2O	H_2O	H_2O	NMP-20% H_2O	TMU-20% H_2O	DMF-20% H_2O	H_2O	35% H_2O	TMU-20% H_2O
0	39.2	40.2	45.7	39.3	48.8	48.7	48.0	52.8	57.2	56.4
20	33.1	32.9	38.2	34.2	44.0	43.5	42.2	48.9	51.0	52.4
40	30.7	30.1	33.6	30.5	41.2	40.8	37.4	47.3	47.3	48.4
60	28.7	26.9	27.6	28.5	38.4	37.7	33.2	45.4	44.3	45.7
90	25.6	22.2	25.6	25.0	35.0	33.0	27.5	41.2	40.3	41.6
120	22.4	18.8	22.2	21.8	31.9	28.8	23.6	39.8	36.9	38.0
180	12.4	13.2	18.4	18.8	24.2	21.1	18.6	32.2	32.4	28.4
240	8.7	9.8	15.8	16.4	18.7	18.5	13.0	28.7	27.0	23.0
CO₂ Removal										
1st 20 minutes	6.1	7.3	7.5	5.1	4.8	5.2	5.8	3.9	6.2	4.0
Av/10 min(3 hr)	1.5	1.5	1.5	1.1	1.4	1.5	1.6	1.1	1.4	1.5
Total CO₂ stripped	30.5	30.4	29.9	22.9	30.1	30.2	35	24.1	30.2	33.4
% regenerated	77.8	75.6	65.4	58.2	61.6	62.0	72.9	54.3	52.8	59.2
Fraction Available to 0.50% CO₂ Effluent										
After stripping	24.3	28.2	21.2	20.6	25.3	27.4	31	12.3	10	22
Initial loading	33	38	37	37	44	44	44	41	37	45

Note: The conditions were a boiling-water bath at 1 atm, using air as the carrier gas, a flow rate of 3 l/min over the liquid surface. V_g/V_s refers to CO_2 in at the time given.

V_g/V_s of the 4N aqueous MEA represents the equilibrium loading (influent CO_2 at 1.0%) under the conditions of the test, rather than the fully carbonated sample (influent CO_2 at 100%). On that basis, the amine-organic solvent-H_2O solutions strip more efficiently than their aqueous analogs.

This table also lists the loading to the breakthrough level of 0.5% CO_2 available after stripping for each mixture. For example, the amount of CO_2 takeup available for a stripped 5N MPA-TMU-H_2O composition was 27 V_g/V_s units, but for stripped aqueous MPA, it was only 12 units. Therefore, the replacement of aqueous MPA by a TMU-MPA-H_2O composition increased the effectiveness of the cycle's absorption phase more than two-fold. With DGA, TMU also increased the effectiveness more than twofold. The MEA-NMP-H_2O combination resulted in a significant improvement over aqueous MEA in this respect.

In summary, the addition of appropriate solvents, such as TMU and Sulfolane, may not only aid stripping but also significantly improve the CO_2 absorption phase of the cycle.

3-(METHYLSULFONYL)PROPYLAMINE

A new amine, 3-(methylsulfonyl)propylamine, $CH_3SO_2CH_2CH_2CH_2NH_2$, was prepared by oxidizing 3-(methylthio)propylamine to the sulfone with hydrogen peroxide or potassium permanganate (6). The literature states that this compound is strongly alkaline, cannot be steam distilled, and can be distilled at 165 to 168°C at 6 mm without decomposition (7).

Figure 18 compares the absorption rate of 3-(methylsulfonyl)propylamine (hereafter designated as MSP) with MEA. The absorption rate of MSP was superior to MEA until 70% of the amine's CO_2 capacity was filled. MSP foamed considerably more than MEA. Addition of foam suppressants reduced the absorption efficiencies of both MSP and MEA, but with MSP the absorption rate equaled that of MEA for the same column foam height. The total CO_2 capacity of MSP is approximately 90% of MEA's at the same conditions and normalities.
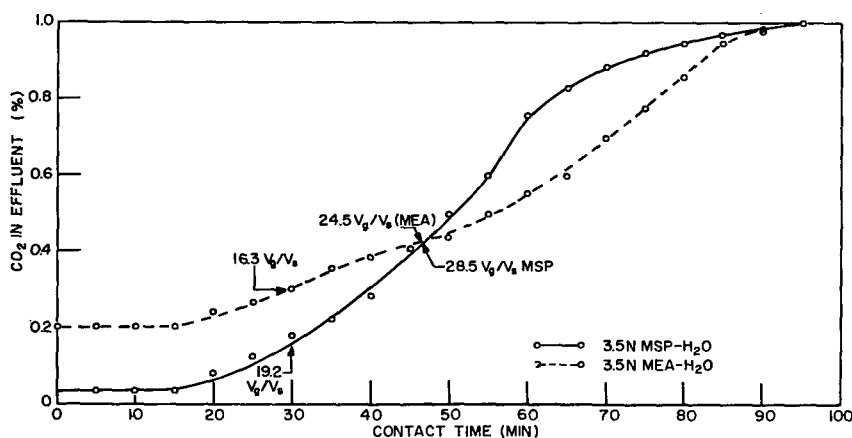
Fig. 18 – CO_2 absorption rate of MEA and MSP, using a flow rate of 3.3 1/min of 1% CO_2 in air at 88°F, 100% R.H., and 1 atm. There were no additives.

On heating, carbonated MSP evolves more CO_2 than MEA (Fig. 19). In 30 minutes MSP lost 27 V_g/V_s units, while MEA evolved only 22 units. The percent regeneration was 92% for MSP but only 76% for MEA. Higher temperatures would probably continue to favor the MSP stripping rate.

The beneficial effect of the nearly complete regeneration of MSP is shown by comparing Figs. 18 and 20. The normalities of both solutions in Fig. 20 are lower than those in the initial absorption run (Fig. 18) because of sampling. This would reduce the breakthrough time about 10%.

Fig. 19 - Stripping properties of MEA and MSP, using a N_2 purge gas over the liquid surface at a flow rate of 500 cc/min at 1 atm. A 50-ml sample was used in an oil bath at 125°C.

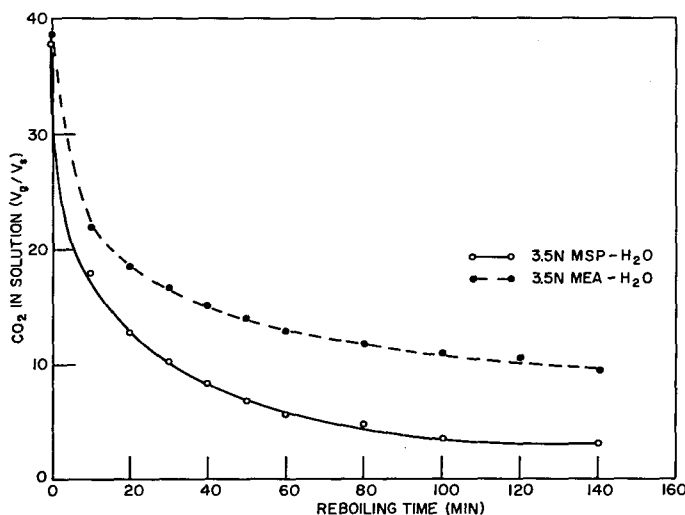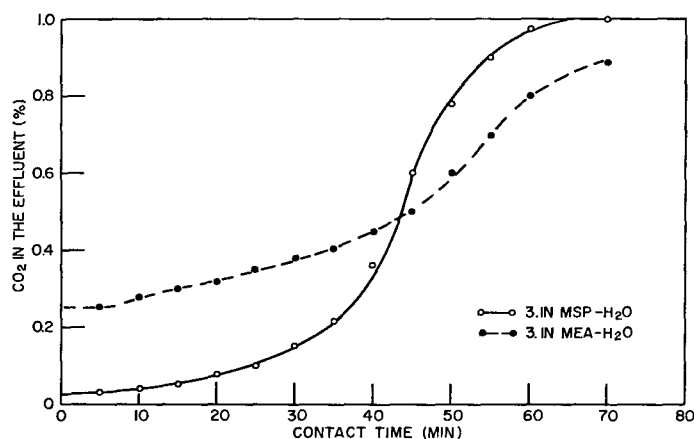Fig. 20 - Effect of initial stripping cycle on second absorption cycle, using a flow rate of 3.3 1/min of 1% CO_2 in air at 88°F and 100% R.H. at 1 atm

The 0.4% CO_2 effluent level obtained after 45 minutes contact time with fresh MEA (Fig. 18) was reached in 39 minutes (corrected to 3.5N) for stripped MEA. With stripped MSP, the absorption rate remained high and did not reach the 0.4% breakthrough value until 45 minutes (same 3.5N correction) compared with 46 minutes for fresh MSP. Thus, the effectiveness of stripped MSP is nearly equal to that of the original amine, while stripped MEA retains only 88% of its original activity.

The oxidation stability of MSP is high relative to that of MEA (Fig. 21). The only significant evolution of ammonia by MSP occurred after 4 days, and this rate was about 1/14 (7%) the evolution rate by MEA for the same period. The normality of MSP and MEA at the start of the oxidation test was 1.4N. After 6 days, the normality of MSP was essentially unchanged (1.38), but the MEA normality had dropped to a value of 1.18. This amounts to a decrease in alkalinity of almost 16% for MEA and only 1.4% for MSP.
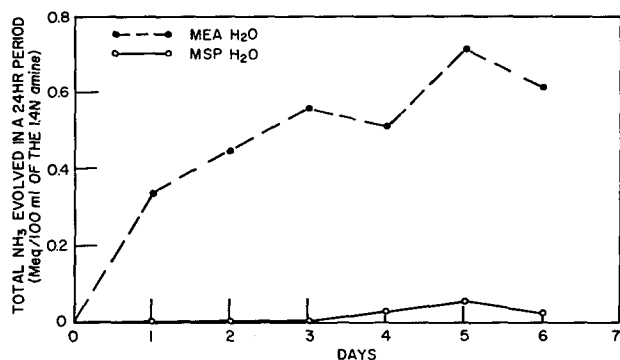
Fig. 21 - Dynamic test of MSP stability with no additive present, using a flow rate of 100 ml/min of 2% CO_2 in air at 55°C

Table 8 summarizes MSP properties with regard to volatility, CO_2 absorption rate, CO_2 capacity, stripping rate, and oxidation stability relative to MEA. The main disadvantage of the sulfone amine is foaming; this can be reduced with suitable antifoam emulsions.

Table 8
Comparison of Amines

	MEA	3-(Methylsulfonyl) propylamine
Volatility	High (760 mm at 170°C)	Low (6 mm at 168°C)
CO_2 absorption rate	1	1.2 × MEA
CO_2 capacity	1	0.9 × MEA
Stripping rate	1	1.2 × MEA
Oxidation stability resistance	Poor	High

Another possible sulfone amine that should possess the desirable properties of MSP, such as low vapor pressure, high thermal stability, and high oxidation resistance, and would probably resist foaming is the methylamino analog of Sulfolane (more appropriately termed 3-(methylsulfonyl)tetramethylene sulfone).

The aminoalkyl sulfones, such as MSP, when they become commercially available, offer possibilities of significant improvement over the current amines now in use. The triliquid concept, regenerative amine-organic solvent-H_2O, also offers an improvement over the aqueous amine systems. In particular, the MEA-Sulfolane-H_2O, MPA-Sulfolane-H_2O, and DGA-Sulfolane-H_2O compositions show promise of possible submarine application.

CONCLUSIONS AND FUTURE PLANS

The three-component system for CO_2 absorption gave preliminary results which indicate that improvements over the present H_2O-amine system could be obtained in the submarine scrubber. The higher rate of stripping than that found for the amine-H_2O system would reduce the CO_2 in the lean liquid, which, in turn and by better absorption, would reduce the CO_2 level in the submarine atmosphere. The combination of two absorption towers (increasing the air being treated) and one stripper in the submarine scrubber could possibly result in approaching the 0.5% CO_2 level recommended as a maximum for submarine atmospheres. The three-component systems, after a more complete study of those containing Sulfolane, will be compared and the better ones recommended for evaluation on the pilot-size stripper unit under study at NRL.

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Chapter 6

COMPATIBILITY OF HOT CARBON DIOXIDE GAS AND DICHLORODIFLUOROMETHANE WITH MOLECULAR SIEVES 5A AND 13X

Elmer T. Johnson

INTRODUCTION

Many proposals have been made for systems that use molecular sieves 5A and 13X to remove CO_2 from environmental atmospheres (1-7). The principal difficulty encountered with these systems is applying heat to the sieve for the thermal regeneration cycle. The method usually used is to embed and/or surround the sieve bed with resistance heaters. With this type of heating, the thermal distances must be kept very short due to the poor thermal conductivity of the sieve. Short thermal distances indicate large surface areas of heaters, which, in turn, indicate bulkier beds, poor gas flows, and increased pressure drops. Also for an increased rate of heat transfer, the thermal gradient should be as large as possible, but hot spots must be avoided because the molecular sieve is thermally stable only to about 538°C (8).

A more efficient and rapid method of raising the temperature of a sieve bed would be to pass a hot gas through the bed. In a submarine system, the most practicable gas for this purpose would be CO_2. A method using this principle has been proposed by Musick and Smith (1). The use of this method, however, results in the sieve being exposed to pure CO_2 at temperatures up to the maximum regeneration temperature. Since the proposed molecular sieves contain calcium or sodium as an essential part of their structure, it was necessary to determine if there would be an irreversible reaction of these elements with hot CO_2 that might destroy the molecular sieve structure and, consequently, the efficiency of the sieves as CO_2 absorbents.

In addition to the above, submarine atmospheres usually contain some halogenated hydrocarbons, especially those used as refrigerants. Some halogenated hydrocarbons have been found to decompose on a molecular sieve (9); and if halogen acids were formed in, or on, the sieve, it is very likely that a reaction would occur which would affect subsequent CO_2 absorption. The possibility of such a reaction occurring was investigated using dichlorodifluoromethane (R-12) as the test gas.

To monitor any changes in sieves under these various conditions, a thermobalance was used. The thermobalance used for these experiments is an instrument which can detect and record changes in the mass of a substance being heated or cooled as a function of temperature or time (in case the substance is maintained isothermally), while maintaining any of a variety of atmospheric environments.

Approximately 100-mg samples of sieve were placed in the thermobalance, and the sample weight was continuously recorded as the temperature was cycled from room temperature to 500°C, while maintaining the desired atmosphere. One-hundred-percent CO_2 was always used to determine any capacity change for both the CO_2 and the R-12 compatibility runs. Any gain or loss of weight corresponded to the absorption or desorption of CO_2. Molecular sieves with pore opening diameters of 5 and 10 Å, from two manufacturers, were used in these tests.

The exposure of the sieves to CO_2 was made directly in the thermobalance; the exposures to R-12 were made in a separate furnace. CO_2 capacity runs to check for damage were subsequently made in the thermobalance. The concentrations of R-12 used were several times greater than would normally be encountered in a submarine in order to accelerate the tests.

In the R-12 compatibility tests, reaction damage was assessed in relation to the capacity of the sieves for CO_2. As in the thermal tests with CO_2, capacity measurements were made in pure CO_2 in the thermobalance. In the 5A sieve tests, dry air containing various concentrations of R-12 was passed through a bed of the molecular sieve contained in a separate furnace and exited into an R-12 infrared analyzer. The incoming gas passed through a preheater and then through the sieve bed, which was also enclosed in a heater. The bed was 7 inches long and 0.15 square inches in cross-sectional area. The temperature of the gas and the bed was raised, and the exit gases were monitored for R-12 content.

The 13X sieve compatibility runs were similar with the exception that the effluent gas was not monitored. Therefore, only the CO_2 capacity of the sieve was determined at the end of the run.

The results of the tests for CO_2 compatibility are shown in Table 9. There was very little change in capacity on 5A or 13X sieves. Sieve 5A is the calcium form with a pore opening diameter of 5 Å. Both 5A sieves lost in capacity for absorbing CO_2; one sample lost

$$\frac{12.8 - 12.7}{12.8} \times 100 = 0.8\%;$$

and the other lost

$$\frac{15.2 - 15.0}{15.2} \times 100 = 1.3\%.$$

Sieve 13X is the sodium form with a pore opening diameter of 10 Å. One 13X sieve gained

$$\frac{16.7 - 15.8}{15.8} \times 100 = 5;7\%$$

and the other lost

$$\frac{18.8 - 18.1}{18.8} \times 100 = 3.7\%$$

in capacity. Part of this variation, 1.6 to 2.5%, could be accounted for in the apparent weight changes encountered, which were in reality due to differences in bouyancy from CO_2 diffusing into or out of the balance chamber during a given run. Corrections for variations in room temperature and pressure would account for a small amount of these differences.

Very long periods of time are required using gas at room temperature to cool the sieve to room temperature equilibrium. Therefore, on cooling and absorbing cycles that did not extend over a night or a weekend, the temperature reached by the sieve could be as much as 5°C above room temperature. This temperature variation would give a

Table 9
Changes in CO_2 Absorption Capacity

Exposure Sequence	Manufacturer X				Manufacturer Y			
	5 Å		10 Å		5 Å		10 Å	
	Cycles	Wt Change* (%)	Cycles	Wt Change* (%)	Cycles	Wt Change* (%)	Cycles	Wt Change* (%)
Dry CO_2, 24°C to 500°C	5	15.2	6	15.8	2	12.8	9	18.8
H_2O-CO_2, 24°C to 500°C	7	–	7	–	5	–	18	–
Dry CO_2, 24°C to 500°C	2	15.0	4	16.7	10	12.3	2	18.1
H_2O-CO_2, 24°C to 500°C	–	–	–	–	2	–	2	–
Dry CO_2, 24°C to 500°C	–	–	–	–	19	12.7	8	18.1

*These figures represent the relative absorption capacity for CO_2 under test conditions.

capacity difference of 0.03 wt-%/°C at 760 mm Hg partial pressure of CO_2 for sieve 5A (10). Corresponding data are not available for sieve 13X. Day-to-day variations in atmospheric pressure would also be reflected in the partial pressure of the CO_2 over the sieve on a given day and would account for a difference of 0.03 wt-%/10 mm Hg CO_2 at 25°C for sieve 5A (10) and a difference of 0.02 wt-%/10mm Hg CO_2 at 25°C for sieve 13X (11). The data in Table 9 have not been corrected for these variations in room temperature and pressure.

With molecular sieve 5A, some decomposition of the R-12 appeared at 225°C, and the decomposition rate increased very rapidly with increased temperature, until 100% decomposition was occurring at 315°C in a dry air stream containing 5000 ppm R-12 at a flow rate of 100 cc/min. Eventually, with a given sample of sieve 5A, the decomposition rate of R-12 would decrease at constant temperature until the R-12 was coming through the bed essentially unchanged. A sample of such a sieve, when removed and examined, appeared to be unchanged. However, when placed in the thermobalance and subjected to CO_2, the sample would neither absorb CO_2 nor outgas any absorbed gas, even after being subjected to a regeneration cycle by heating to 500°C.

Molecular sieve 13X was placed in a stream of air containing about 1% R-12 for a period of 12 hours at 300°C. The sieve was then removed and placed in the thermobalance, and CO_2 was introduced while cycling between room temperature and 500°C. This R-12 treatment reduced the pure CO_2 capacity of this sieve from 16 wt-% to 10.0 wt-%.

CONCLUSIONS AND FUTURE PLANS

There appears to be no degradation of molecular sieves 5A and 13X in a pure CO_2, air-CO_2, or CO_2-H_2O environment at temperatures up to 500°C. Molecular sieves 5A and 13X are destroyed in mixtures of air with 0.5 to 1.0% R-12 at temperatures above 225°C.

Future work will be concerned with the sieves being exposed to R-12 and moisture at room temperature and then back-flushing with air that is being heated from room temperature to 316°C to see if the R-12 will be removed before degradation begins. To investigate the possibility that halogenated hydrocarbons may accumulate in the stock tank of CO_2 used for heating the sieve, an experiment is planned for passing R-12 and CO_2 over the sieve at 150°C and examining the sieve for degradation.

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Chapter 7

THE DEVELOPMENT OF A NONTOXIC, SELF-EXTINGUISHING PAINT FOR THE INTERIOR OF NUCLEAR-POWERED SUBMARINES

T. R. Walton

INTRODUCTION

Earlier reports (1-5) describe the background and previous progress in this program. In brief review, the Navy needs a fire-retardant paint for use in the interior of nuclear-powered submarines that will release little or no toxic materials into the atmosphere during and after application. In addition, the paint should meet the usual high standards of quality and appearance.

The paint must be free of volatile toxic materials, because, as a practical matter, paints cannot be applied in operating submarines early enough to allow all paint solvents to escape to the outside atmosphere before the submarine goes on patrol and is sealed. The retention of small amounts of residual solvents in conventional paint films from several to many days after painting has been established (6) and can constitute a health hazard.

Fire retardancy is required to eliminate the dried paint film as a source of propagation in the spreading of fires. Since these paints are generally used on noncombustible substrates, the burning behavior of the dried film itself, and not its ability to protect a combustible substrate, is of most concern.

The properties and performance required of this paint are summarized in Table 10. In general, the paint should exhibit at least the minimum performance of the solvent-based chlorinated alkyd paint (Formula 124/58, MIL-E-17970C) (7) that is normally used when sufficient ventilation is possible before submergence.

Regardless of the outboard ventilation possible after the application of this chlorinated alkyd paint, it cannot be used during the 5 days preceding the submarine's departure on patrol (8). Because there is generally a large amount of painting to be completed during this 5-day period, three proprietary, fire-retardant, water-based paints have been approved for use during this period (9). Unfortunately, these proprietary paints are quite inferior to the chlorinated alkyd and are undesirable for such widespread use. Thus, a program was initiated at NRL to develop a high-quality paint for use during this 5-day interval and, hopefully, even under sealed-ship conditions. This latter capability would allow much of the interior painting to be done by the ship's personnel after the submarine has departed on its patrol.

In the last annual report (5), four experimental paints were discussed. In three of these formulations efforts were made to combine decorative, functional, and fire-retardant properties into a single paint. Water was used as the solvent, thus reducing the volatile organic content; antimony oxide and a chlorine source were included to obtain fire retardancy. The fourth paint uses a different approach to a fire-retardant coating. In this approach an undercoat provides the fire-retardant component in the system, while a top-coat, although in itself combustible, provides the requisite decorative qualities. The

Table 10
Performance Requirements of a Submarine Interior Paint

Property	Requirement
Nontoxic	The paint should contain little or no volatile organic solvents or toxic additives.
Fire retardancy	The paint burns when exposed to a flame but should immediately self-extinguish when the source of ignition is removed.
Gloss, 60°	35 to 50%.
Leveling	A value of 7 or better using the NYPC test method, in order that a reasonably smooth and attractive appearance void of brush marks is obtained.
Hiding	Qualitatively, the paint should provide good hiding in two coats and preferably in one coat.
Flexibility	The dry paint film should be sufficiently flexible to permit application to flexible poly(vinyl chloride) foam insulation without cracking.
Drying time	Two hours or less.
Scrubbability	A 2- to 3-mil-thick film should withstand 4000 oscillations on the Gardner Washability Machine using an abrasive cleansing solution.

fire-retardant additives, which were responsible for the poor appearance of the paint, can thus be confined to the undercoat, which is then hidden by the topcoat, while the system remains fire retardant.

DISCUSSION

Latex/Halogenated Plasticizer Paints

The latex/halogenated plasticizer paints are based on Rohm and Haas' Rhoplex AC22X acrylic emulsion and titanium dioxide pigment. Antimony oxide, a chlorinated rubber dispersion, and a chlorinated paraffin dispersion were used as the fire-retardant additives. Except for its low gloss (7%), one formulation fairly well meets the requirements outlined in Table 10. However, as reported in the last annual report (5), the manufacturer of the chlorinated rubber dispersion has decided against its further commercial production. This component is critical to the formulation in that it has the least adverse effect on the normal properties of the paint. Since another source of this fire-retardant additive or a suitable substitute has not been found, further work with this coating has been discontinued.

Convertible, Water-Soluble, Chlorinated Alkyd Paints

As discussed in the last annual report (5), further work on the water-soluble, chlorinated alkyd paints was discontinued.

Water-Soluble Linseed-Oil/Halogenated
  Plasticizer Paints

As discussed in the last annual report (5), further work on the water-soluble linseed-oil paints was discontinued.

The Two-Coat, Fire-Retardant Paint System

The two-coat, fire-retardant paint system is presently the only coating now under development. Efforts to develop a single coating to meet the performance requirements summarized in Table 10 have encountered difficulties because of the adverse effects the fire-retardant additives have had on paint properties, such as gloss, leveling, hiding, and appearance. Thus, as an alternative to the single-coat approach, a two-coat system was devised in which the first coat, or undercoat, would impart fire retardancy to the system, and the second coat, or topcoat, would provide the decorative qualities. In this manner, the fire-retardant additives can be confined to the undercoat, which is concealed by the decorative topcoat. Although the topcoat alone might be combustible, in combination with the fire-retardant undercoat, the total system is self-extinguishing.

The undercoat and topcoat formulations discussed in the last annual report (5) have been modified to reduce a strong pine oil and ammonia odor and to improve leveling and brushing. The new formulations are shown in Tables 11 and 12. The main changes are the deletion of Amberlac 165 (a wetting agent), the pine oil (a defoamer), and Acrysol G-110 (a thickening agent), whereas Triton GR-5 (a wetting agent) and Bubble Breaker 746 (a defoamer) have been added. Propylene glycol has been increased in the topcoat and added to the undercoat. Ten gallons each of this fire-retardant undercoat and decorative topcoat have been prepared for shipboard evaluation.

Both the fire-retardant undercoat and the decorative topcoat were formulated to contain a minimum of volatile organic additives. Propylene glycol (5.0% in the undercoat and 5.4% in the topcoat) is the major volatile organic additive in both formulations, while approximately 0.04% isopropyl alcohol is introduced into each with the surfactants. Propylene glycol is reported to be completely nontoxic (10,11), even when taken internally. Isopropyl alcohol is present in such small quantities, approximately 2 g/gal, that the 24-hour exposure limit of 200 ppm would never be reached even if 2 gal of the paint were accidentally spilled in a small, isolated compartment. At present, however, it is recommended that this paint not be used under sealed-ship conditions, because the ingredients are commercial materials which could be contaminated with undesirable byproducts not removed in manufacturing. Until this coating system is shown to be an acceptable replacement for the three proprietary fire-retardant paints through actual field testing on submarines, it would not be practical to carry out a detailed analysis on the numerous ingredients. If field testing supports use of this coating system and a detailed analysis shows it to be unsuitable for use on patrol because of volatile toxic contaminants, it is quite possible that appropriate substitution or simple purification of the offending ingredient(s) could be made. But even if this coating system could not be used under sealed-ship conditions (that is, on patrol), its superior performance would recommend its use over the presently used proprietary paints.

To support this view, a comparison of the properties and performance of the three proprietary paints and the NRL system is made in Table 13. Data on the standard Navy chlorinated alkyd paint are also included.

The three proprietary materials require at least two to three coats for complete hiding. The NRL coating normally gives complete hiding with one coat each of the undercoat and topcoat. Both Ocean 634 and Amercoat 1768 produce a very low gloss. Although

Table 11
The Formulation (N4001-69) of the NRL
Fire-Retardant Undercoat

Ingredients	Supplier	Weight-Percent
Water		13.748
Propylene glycol, U.S.P.	Fisher Scientific Co.	4.979
Tamol 731 (25% solids)*	Rohm & Haas	1.178
Triton CF-10	Rohm & Haas	0.119
Nopco NDW	Nopco Chemical Co.	0.119
G-11 (hexachlorophene, U.S.P.)	Sindar Corp.	0.040
Antimony oxide, KR grade	Harshaw	16.511
Eldefoam	Foremost Chem. Prod. Co.	0.295
Polyglycol P1200	Dow	0.297
Triton GR-5 (60% solids)†	Rohm & Haas	0.189
Rhoplex AC-22X (44.5% solids)‡	Rohm & Haas	33.501
Rhoplex C-73 (46.5% solids)‡	Rohm & Haas	3.183
Delvet 65 (65% solids)§	Diamond Alkali Co.	25.627
Bubble Breaker 746	Balab	0.214
Total		100.000

*Aqueous solution.
†Aqueous solution containing 20% isopropyl alcohol.
‡Aqueous dispersion, contains no mercury preservative.
§Aqueous dispersion.

Density 10.91 lb/gal
PVC 10.76%
Wt-% solids 50.75
Wt-% volatile organics 5.017

the gloss of the Devflex MD 2707 is better, it is still inferior to the 42% gloss of the NRL system. All three proprietary paints show brush marks when applied by brushing, and although the Devflex is better than the Ocean 634 and Amercoat 1768, it is poorer than the NRL system. All four paints dry in 1 to 4 hours; however, the Devflex MD 2707 and Ocean 634 have a slight after-tack that is present for several weeks after application. The NRL coating is superior in freeze-thaw stability and scrub resistance. The adhesion of the NRL system, the Ocean 634, and Amercoat 1768 was evaluated on cold-rolled steel panels treated with wash primer (Formula 117, MIL-P-15328). By scratching the dried coatings with the fingernail, the NRL coating system (one coat undercoat and two coats topcoat) displayed much better adhesion than either proprietary paint. This qualitative evaluation was confirmed using the Arco Microknife Test (12) in which the NRL system had an adhesive value of 2.29 (best), Ocean 634 had a value of 5.67, and Amercoat 1768 had a value of 6.12 (poorest).

Table 12
The Formulation (N4001-67) of the NRL Decorative,
Combustible Topcoat

Ingredients	Supplier	Weight-Percent
Water		10.076
Tamol 731 (25% solids)*	Rohm & Haas	2.105
Propylene glycol, U.S.P.	Fisher Scientific Co.	5.420
Triton CF-10	Rohm & Haas	0.188
Nopco NDW	Nopco Chemical Co.	0.188
G-11 (hexachlorophene, U.S.P.)	Sindar Corp.	0.091
Titanium dioxide, R-900	DuPont	29.633
Eldefoam 2892	Foremost Chemical Co.	0.462
Polyglycol P1200	Dow	0.463
Triton GR-5 (60% solids)†	Rohm & Haas	0.195
Rhoplex AC-22X (44.5% solids)‡	Rohm & Haas	45.939
Rhoplex C-73 (46.5% solids)‡	Rohm & Haas	4.909
Bubble Breaker 746	Balab	0.331
Total		100.000

*Aqueous solution.
†Aqueous solution containing 20% isopropyl alcohol.
‡Aqueous dispersion, contains no mercury preservative.

Density 11.42 lb/gal
PVC 26.33%
Wt-% solids 54.26%
Wt-% volatile organics 5.459

A more detailed report (13) on the NRL system has been prepared and provides extensive information on the fire-retardant performance of these coatings. Only the more significant data will be summarized in this report. The test procedure has been described (13) and will be only briefly outlined here. The paints are applied to an asbestos paper (16 mils thick) or aluminum foil (0.8 mil thick) substrate with a film caster or a brush. After the films have dried for at least 5 days, the coated area is cut into 1-by-11-inch-long test strips. The test sample is ignited with a microburner, which is then extinguished, and the time is measured for the sample either to self-extinguish or burn a 6-inch length.

Tables 14 and 15 show the performance of the NRL system and the three proprietary paints on asbestos substrates. The film caster clearance is used as a measure of film thickness because of the difficulty in measuring the dry-film thickness on the asbestos substrate with a micrometer. However, these paints will yield dry films of approximately the same thickness when similarly applied. (The dry-film thickness for these coatings applied with the 12-mil caster is approximately 2.8 mils). With a 12-mil topcoat applied over a 6-mil undercoat, the NRL system is immediately self-extinguishing. This performance is superior to the three proprietary paints at similar film thicknesses; none of these immediately self-extinguished.

Table 13
Performance of Interior Paints for Nuclear Submarines

Properties	MIL-E-17971C Formula 125/58 (Chlorinated Alkyd)	Devflex MD 2707	Amercoat 1768	Ocean 634	NRL Undercoat Formulation N4001-69	NRL Topcoat Formulation N4001-67	NRL System*
Hiding (qualitative)	Good-excellent	Fair†	Fair†	Fair†	Poor	Good	Good
60° gloss (Gardner)	35-50%	32%	23-32%	9%	5%	42%	42%
Leveling (NYPC test blade)	–	6 (Good)	5 (Fair)	0 (Poor)	6 (Good)	6 (Good)	–
Flexibility on elastomeric plastic insulation	Cracks	Does not crack	Does not crack	Does not crack	Does not crack	Does not crack	Does not crack
No. of freeze-thaw cycles passed	Stable	0	>2	0	Will pass a few cycles	Stable	–
Scrub resistance	3500	1450	850	1300	–	2550	–
Drying time (hr)	2-7	1	1-2	1	1-2	1-4	–
Adhesion (Ref. 12)	–	–	6.12 (worst)	5.67	–	–	2.29 (best)

*This system consists of one coat of the NRL undercoat and two coats of the NRL topcoat.
†At least two coats are needed for complete hiding.

Table 14
Evaluation of Fire-Retardant Paints on Asbestos Paper Substrate

Coating*	No. of Samples	Results†
Ocean 634	4	SE‡ after 4.1 sec
Amercoat 1768	4	SE after 5.4 sec
Devflex MD 2707	1	Burned completely in 25.1 sec
	3	SE after 1.5 sec
12 mil DCT§/6 mil FRU#	4	All immediately SE

*The film was applied with a 12-mil caster clearance unless otherwise shown.
†The average time the sample burned after the ignition torch was turned off.
‡SE = self-extinguished.
§NRL decorative, combustible topcoat.
#NRL fire-retardant undercoat.

Increasing the film thickness by using a 20-mil caster clearance resulted in decreased performance for all four coatings. However, the NRL system is still very good with three out of the four samples tested immediately self-extinguishing and the fourth sample self-extinguishing after 1.8 sec. The three proprietary paints were much poorer, with most of the samples burning completely.

Table 16 summarizes the performance of these coatings on aluminum foil. Because of its uniformity, aluminum foil has the advantage that accurate dry-film thicknesses can be measured. The aluminum foil also provides a severer test than the asbestos substrate. Except for very thin films of the Devflex MD 2707 paint, the proprietary paints were completely combustible. (Even two out of the five thin Devflex samples burned completely.) In the case of the NRL system, it was found that if the film thicknesses of the topcoat and the undercoat were kept close to a 1-to-1 ratio, good fire retardancy was maintained. (In the case of the asbestos substrate, a ratio of 2-to-1 could be tolerated without appreciably decreasing the fire retardancy of the system.) Even with three applications of the NRL system, where each application consisted of one coat of the fire-retardant undercoat and one coat of the decorative topcoat, the fire-retardancy performance

Table 15
Evaluation of Fire-Retardant Paints on Asbestos Paper Substrate

Coating*	No. of Samples	Results†
Ocean 634	3	Burned completely in 35.8 sec
	1	SE‡ after 1.0 sec
Amercoat 1768	4	Burned completely in 34.5 sec
Devflex MD 2707	2	Burned completely in 15.7 sec
	1	SE after 1.6 sec
	1	Immediately SE
20 mil DCT§/10 mil FRU#	1	SE after 1.8 sec
	3	Immediately SE

*The film was applied with a 20-mil caster clearance unless otherwise shown.
†The average time the samples burned after the ignition torch was turned off.
‡SE = self-extinguished.
§NRL decorative, combustible topcoat.
#NRL fire-retardant undercoat.

Table 16
NRL Evaluation of Fire Retardant Paints
on Aluminum Foil Substrate

Coating	Film Caster Clearance or No. of Brush Coatings	Dry Time (days) (Ambient Conditions)	Dry-Film Thickness	No. of Samples	Results
Ocean 634	10 mils	21	2.8	5	Burned; 10.3 sec
Amercoat 1768	10 mils	21	3.1	5	Burned; 9.5 sec
Devflex MD 2707	10 mils	21	2.9	5	Burned; 11.5 sec
Ocean 634	1 brush coating	21	0.9	5	Burned; 4.4 sec
	2 brush coatings	20	1.7	5	Burned; 7.5 sec
	3 brush coatings	18	2.5	5	Burned; 10.1 sec
Devflex MD 2707	1 brush coating	21	0.7	2	Burned; 3.9 sec
	1 brush coating	21	0.7	1	SE after 1-2 sec
	1 brush coating	21	0.7	2	Immed. SE
	2 brush coatings	20	1.6	5	Burned; 6.7 sec
	3 brush coatings	18	2.4	4	Burned; 8.9 sec
NRL Coating System (DCT*/FRU†)					
(2.4/1.4)‡	10 mils/brush	20	3.8	4	Burned; 12.6 sec
		20	3.8	1	SE after 1.5 sec
(0.8/1.4)	All brush	21	2.2	4	Immed. SE
		21	2.2	4	SE after 1.2 sec
(0.9/1.2) (0.9/1.2)	All brush	20	4.2	3	SE after 1.5 sec
		20	4.2	2	Immed. SE
(1.2/1.2) (1.0/0.9) (0.6/1.1)	All brush	18	6.0	4	SE after 1.4 sec
DCT/DCT/FRU					
(0.8/1.5/1.0)	All brush	20	3.3	3	Burned; 10.5 sec
		20	3.3	1	SE after 2.0 sec

*Decorative combustible topcoat.
†Fire-retardant undercoat.
‡Individual dry-film thicknesses.

was quite acceptable with two out of six samples immediately self-extinguishing and the remaining four self-extinguishing in approximately 1.4 sec.

The fire-retardancy of the NRL system was also evaluated by the Mare Island Paint Laboratory (14). At Mare Island, the flammability of paints is evaluated thermoelectrically by a test which determines if a paint will ignite into flame when the sole ignition source is the metallic substrate to which the paint adheres. The test is essentially the same as described by Birnbaum and Markowitz (15). A 15-mil-thick steel specimen coated on both sides with the paint is rapidly heated to approximately 1800°F in 60 sec by passing a large current through it. The specimen is observed to see if the paint ignites, flashes, or burns.

The results from Mare Island are reported in Table 17. The Amercoat 1768 was not tested, because Mare Island was unable to obtain this paint. The importance of applying only one coat of the NRL topcoat over a single coat of the fire-retardant undercoat is apparent. With a single topcoat, none of the three specimens ignited; with two or three topcoats, all samples ignited and burned for 12 sec (two topcoats) and 49 sec (three top-coats). However, if the fire-retardant undercoat is used beneath each topcoat, as many as three applications of the topcoat and undercoat can be made (a total of six coats) and still maintain an acceptable fire-retardancy performance. Under these conditions, one sample did not ignite, and two ignited after 89 sec and burned for 24 sec. This performance is better than the Ocean 634, whose samples ignited after 60 sec and burned for an average of 27 sec. The performance is not as good as the Devflex MD 2707, where all three samples failed to ignite; however, it should be noted that the coating thickness of the Devflex sam-ples was only 5.5 mils, while the NRL system was 8.0 mils. If the Devflex samples were 8 mils thick, it is quite likely that their performance would be no better than the six coats of the NRL system.

Table 17
Summary of Mare Island Paint Laboratory's Evaluation of Fire
Retardant Paints on Thermoelectric Tester (Metal Substrate)

Coating*	Avg Dry-Film Thickness (mils)	No. of Samples	Results
Ocean 634	5.3	3	Burned 27 sec (ignited at 1800°F)
Amercoat 1768	–	–	Not tested
Devflex MD 2707	5.5	3	No ignition
NRL Coating System ·			
1 coat DCT/1 coat FRU	2.7	3	No ignition
2 coats DCT/1 coat FRU	4.3	3	Burned 12 sec (ignited after 84 sec)
3 coats DCT/1 coat FRU	5.0	3	Burned 49 sec (ignited after 72 sec)
3 coats (1 coat DCT/1 coat FRU)	8.0	1	No ignition
3 coats (1 coat DCT/1 coat FRU)	8.0	2	Burned 24 sec (ignited after 89 sec)

*The film dried for 30 days at room temperature.

SUMMARY

The studies at NRL and the Mare Island Paint Laboratory have indicated that the NRL two-coat system is at least as good as the three proprietary fire-retardant paints and probably better. The NRL fire-retardant undercoat and the decorative topcoat should be applied at approximately the same dry-film thickness, and if more than one coat is needed, the undercoat should be used between each additional topcoat. In this manner, the coating will exhibit its maximum fire-retardant and decorative qualities, which appear to be superior to the three proprietary paints in all respects. Since propylene glycol was used as the cosolvent in the NRL system, it is expected to be even less toxic than the proprietary paints.

Work on the one-coat, fire-retardant, decorative paint was discontinued because the major fire-retardant additive was no longer available and another source or suitable substitute could not be found.

FUTURE WORK AND RECOMMENDATIONS

No further experimental work is planned for this program. It is recommended that the NRL coating be evaluated on a nuclear-powered submarine to determine the acceptability of this coating in the fleet. Eight gallons each of the fire-retardant undercoat and the decorative topcoat had been prepared for initial evaluation. However, these coatings are now over two years old and are not recommended for a final evaluation because of some deterioration during storage. It is recommended instead that 100 to 200 gallons of new material be procured directly from a paint manufacturer for this shipboard evaluation. If the results are favorable, specifications should be written and the coating system incorporated into the Federal Supply System.

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RECOMMENDATIONS

Slightly over half of the recommendations in the previous report have been implemented to an adequate extent. The current recommendations combine the comments on each of the previous ones with certain new recommendations. All of the following recommendations are addressed to the Naval Ship Engineering Center:

1. The prior recommendation for an expansion of the study on the degradative effect of nuclear-submarine atmospheres on materials has been largely ignored, but this may be due to funding difficulties. The NRL effort is limited both by personnel and funding, but the overall program should still be expanded.

2. The revised Habitability Data Book continues to serve an excellent purpose and should be continually updated as previously recommended.

3. Quality control appears finally to have become adequate for the Mark IV Atmosphere Analyzer, but close and continued inspection is an important requirement.

4. The ion exchange principle advocated in the Ionics, Inc., 10-man prototype CO_2-O_2 system must not be neglected solely because the faulty equipment received inadequate and insufficiently funded evaluation at NSRDL (Annapolis). Further contractor development and evaluation are recommended as soon as funding becomes available.

5. None of the recommended improvements in the CO_2 scrubber system have yet been implemented other than the continuation of NRL research to find an absorbent better than MEA. To repeat, design changes in the scrubber are required to avoid burping of MEA into the atmosphere and to improve stripping efficiency (as demonstrated in the NRL horizontal tube reboiler), battery-grade water should be used in the scrubber, and standardization of the EDTA-VFS additive package should be effected.

6. It appears that chlorinated hydrocarbons are used less, as recommended, but this trend may be reversed if Freon-113 is increasingly used as a cleaning solvent. No Freon-113 should be used in nuclear submarines without immediate subsequent removal from the ship, and no chlorinated hydrocarbons should be used in the submarines without the same immediate removal.

7. Subject to further operational evaluation of the Allis-Chalmers O_2 generator, additional attention should be devoted to other O_2 generating systems at reduced pressures.

8. The NRL-developed paint system for nuclear submarine interiors should receive operational evaluation in a nuclear submarine and then, if satisfactory, should be adopted by the fleet for uniform use.

9. NavSec is commended for the increasing tendency of Navy commands to determine the possible effects of new materials in submarine atmospheres before final commitments are made. However, it is still recommended that further attention and publicity be provided to this critical aspect of providing adequate security to nuclear submarine atmospheres.

Future interests and action of NRL in the field of submarine atmospheric habitability will continue to be guided by the following considerations:

1. All research and development will continue to be performed with the view of applicability toward an integrated air-purification system.

2. Investigations will continue on (a) methods of air sampling and analysis, including infrared, nmr, mass spectrometry, and gas chromatography, (b) the Mark V (chromatographic) Atmosphere Analyzer, (c) the Total Hydrocarbon Analyzer (until the instrument aboard ship provides routine and satisfactory answers), (d) the gas-stripping mechanism in the CO_2 scrubber, (e) possible substitute for MEA in a present or new CO_2 scrubber, (f) reactions, corrosion, and acid absorption in the CO/H_2 burner, and (g) improvement of specifications for burner catalyst.

3. NRL will also continue to provide consultative services to the Naval Ship Systems Command, the Naval Ship Engineering Center, and the Deep Submergence Systems Project as required, as well as to other Navy and government activities concerned with closed environmental systems.

4. As a continuing policy, promising research ideas will be pursued as part of NRL's program.

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13. ABSTRACT

This progress report supplements NRL Reports 5465 of Apr. 21, 1960; 5630 of July 14, 1961; 5814 of Aug. 29, 1962; 6053 of Dec. 31, 1963; 6251 of Mar. 23, 1965; 6491 of Jan. 11, 1967; and 6722 of June 18, 1968, which provided a comprehensive review of the past and present research and development effort of NRL on the atmospheric habitability of submarines. At present, emphasis is being devoted almost exclusively to nuclear-powered submarines, although an increasing effort is being applied to SeaLab, Man-in-the-Sea and other tasks of the Deep Submergence Systems Project. Considerable progress has been made in developing both laboratory and shipboard methods of sampling, analysis, and control, but major shipboard analytical equipment continues to be of marginal quality. Some of the topics covered in the present report include a fire-retardant and nontoxic paint system for application when necessary during submergence, atmospheric contamination with a cleaning solvent, the NRL Total Hydrocarbon Analyzer, catalyzed combustion of various types of atmospheric contaminants, and CO_2 absorption properties of some new amines.

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Atmosphere purification						
Catalytic oxidation						
Carbon dioxide absorption						
Oxygen generation						
Chromatographic analysis						
Mass spectrometric analysis						
Nmr analysis						
Carbon monoxide analysis						
Carbon monoxide removal						
Chlorinated hydrocarbons						